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# DIVALENT CARBON DERIVATIVES AS REACTION INTERMEDIATES

By

JACK HINE

Status Report No. 1-28
Technical Report No. 1-7
Final Report

Project No. A-239
Contract No. DA-01-009-ORD-431
Army Research Office(Durham)Project No. 1452

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
1955 - 62

A-239

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
ATLANTA, GEORGIA

September 23, 1955

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 1
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
June 27, 1955 to September 22, 1955
OOR Project No. 1452
Contract No. DA-01-009-ORD-431

Gentlemen:

Mr. Richard Butterworth, a candidate for the M.S. in Organic Chemistry at Georgia Tech, has been employed as Research Assistant on the project. The work described below was carried out by Mr. Butterworth and the undersigned.

Previous work at Georgia Tech on the relative reactivities of haloform toward basic hydrolysis had involved studies of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$, $CHCl_2I$, $CHCl_2F$, $CHF_3$ and CHBrClF, although only $CHCl_3$ was studied in any considerable detail. The relative reactivities, particularly the great reactivity of CHBrClF had seemed difficult to explain on the basis of the proposed mechanism involving carbon dihalides as reaction intermediates. We have now evolved a hypothesis to explain these data and are in the process of running experimental tests upon this hypothesis. During the current quarter we have studied the effect of added halide ions on the rate of the basic hydrolysis of $CHBrCl_2$ and $CHBr_2F$, and made preliminary measurements on the rates of hydrolysis of $CHBrF_2$ and $CHClF_2$.

Respectfully submitted:

Jack Hine
Project Director

Approved:

Wyatt C. Whitley
Acting Chief
Chemical Sciences Division

A-239

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

December 21, 1955

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
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Subject: Status Report No. 2
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
September 23 to December 20, 1955
OOR Project No. 1452
Contract No. DA-01-009-ORD-431

Gentlemen:

Mr. Richard Butterworth, Research Assistant on the project, has completed the research for his M.S. thesis and is therefore being terminated. The new Research Assistant will be Mr. Norbert W. Burske, a candidate for the Ph.D. in organic chemistry.

A paper on "Divalent Carbon Derivatives as Reaction Intermediates" was presented at the Southeastern Regional Meeting of the American Chemical Society held at Columbia, South Carolina in November.

During the current quarter, studies were made on the effect of added halide ions on the rate of basic hydrolysis of $CHBr_2Cl$. These studies revealed a "mass law effect" (the halide ions decreased the reaction rate) and therefore show that the reaction proceeds through a dihalomethylene intermediate. In line with our previously mentioned hypothesis concerning the effect of structure on the rates of the basic hydrolysis of haloforms, we have studied iodoform and found, as predicted, that it is the second least reactive haloform (fluoroform is the least reactive). Other critical tests of the hypothesis include its predictions that $CDBr_2F$ will undergo deuterium exchange several times faster than it hydrolyzes, that $CDBrClF$ will exchange only very slightly faster than it hydrolyzes and that the hydrolysis of $CDBrF_2$ will be unaccompanied by deuterium exchange. For this reason, these three deuterium compounds have been prepared and we plan during the next quarter to compare their deuterium exchange and hydrolysis rates.

Respectfully submitted,

Approved:

Jack Hine, Project Director

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

March 22, 1956

Commanding Officer
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2127 Myrtle Drive
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Subject: Status Report No. 3
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
December 21, 1955 to March 21, 1956
OOR Project No. 1452
Contract No. DA-01-009-ORD-431

Gentlemen:

The work described below was carried out by Mr. Norbert W. Burske and the undersigned.

The compounds $CHBrF_2$ and $CHClF_2$ were previously found to undergo basic hydrolysis at a considerably faster rate than would be expected from the accepted mechanism for the basic hydrolysis of haloforms:

$$\begin{aligned} CHX_3 + OH^- &\rightleftharpoons CX_3^- + H_2O \\ CX_3^- &\longrightarrow CX_2 + X^- \\ CX_2 &\longrightarrow CO + HCO_2^- \end{aligned} \qquad (I)$$

The great reactivity of these compounds did seem explicable on the basis of a concerted alpha-elimination involving the direct one-step formation of the intermediate carbon dihalide:

$$\begin{aligned} CHX_3 + OH^- &\longrightarrow CX_2 + H_2O + X^- \\ CX_2 &\longrightarrow CO + HCO_2^- \end{aligned} \qquad (II)$$

Haloforms reacting by the latter mechanism (II) should, unlike all haloforms studied heretofore, undergo hydrolysis without concomitant deuterium exchange. It has now been found that the basic hydrolysis of $CDBrF_2$ in $H_2O$ is not accompanied by deuterium exchange. Thus it seems likely that mechanism II is operative in this case.

In order to learn more about the reactivities of haloforms in the various steps of mechanisms I and II, we have also studied the base

catalyzed deuterium exchange of $CD_2ClI$ (much faster than its hydrolysis), $CDBr_2F$ (several times faster than its hydrolysis) and $CDBrClF$ (somewhat faster than its hydrolysis). From these and earlier data we find the following order for the ability of the various halogens to increase reactivity in the carbanion formation of haloforms: $I \sim Br > Cl > F$. It further seems probable that the following order holds for the ability of the various halogens to stabilize carbon dihalide intermediates: $F > Cl > Br > I$.

We hope to bring added evidence to bear on these points during the coming quarter.

Respectfully submitted,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

June 27, 1956

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
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Subject: Status Report No. 4
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
March 21 to June 27, 1956
OOR Project No. 1452
Contract No. DA-01-009-ORD-431

Gentlemen:

Mr. Norbert W. Burske has completed his Ph.D. research and his place as research assistant on the project has been taken by Mr. Stanton J. Ehrenson who is working toward the Ph.D. in physical chemistry at Georgia Tech. The work done with Mr. Burske on the kinetics of the base-catalyzed deuterium exchange of haloforms is being written up for submission to the Journal of the American Chemical Society. The manuscript should be completed this summer, and when it is copies will be sent to the Office of Ordnance Research.

Mr. Ehrenson is studying the effect of solvent changes on the rate of the alkaline hydrolysis of haloforms. His current studies involve the use of aqueous dioxane mixtures of various compositions. The reaction rate is found to increase in general with increasing dioxane content, but the extent of the increase differs for different haloforms. We hope to be able to devise some basicity function, analogous to Hammett's well-known acidity function, $H_0$, that will be useful in correlating the rates of other base-catalyzed reactions in addition to the hydrolysis of haloforms. The results already obtained, however, show that the system is more complicated than those to which the $H_0$ function is applicable.

Respectfully submitted,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

H. 239

September 25, 1956

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 5
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
June 28, 1956 to September 24, 1956
OOR Project No. 1452
Contract No. DA-01-009-ORD-431

Gentlemen:

Most of the work that has been carried out under this contract was described in a talk at the Sixth Biennial Conference on Reaction Mechanisms at Swarthmore, Pennsylvania on September 13, 1956.

Mr. Ehrenson's work on solvent effects, described in the last progress report, has yielded results that defy our attempts at simple explanation. We have, therefore, turned out efforts toward the quantitative correlation of rates of formation of dihalomethylenes by the reaction of haloforms with alkali. For the reaction mechanism

$$CHXYZ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CXYZ^- + H_2O$$

$$CXYZ \xrightarrow{k_2} CXY + Z^-$$

the hydrolysis rate constant, $k_h$, is expressed

$$k_h = \frac{k_1 (k_2/k_{-1})}{1 + (k_2/k_{-1})}$$

Since we have values of $k_1$ available from deuterium exchange data, a correlation of values of $(k_2/k_{-1})$ will give us a correlation of $k_h$'s. In the following linear free energy relationship

$$\log \frac{(k_2/k_{-1})^{CHXYZ}}{(k_2/k_{-1})^{CHCl_3}} = Z_z + \log \frac{n_z}{3} + M_x + M_y + a \log \frac{k_1^{CHXYZ}}{k_1^{CHCl_3}}$$

$Z_z$ is a parameter for the halogen that is lost as an anion in the rate controlling step of the reaction, $n_z$ is the number of halogen atoms of this kind present in the haloform molecule, $M_x$ and $M_y$ are parameters for the halogen atoms that remain behind in the rate controlling step and a is a proportionality factor. The M values are measures of the ability of the various halogens to stabilize the dihalomethylene being formed in the transition state of the reaction. Since only relative values of Z and M are meaningful, chlorine is set as the "reference halogen", $Z_{Cl}$ and $M_{Cl}$ being set equal to zero. We have obtained enough data to show that this equation will work at least fairly well, but we will get more data before determining the optimum values of the various parameters by a least squares treatment.

Respectfully submitted,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

JH/JJ
A-839

December 27, 1956

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 6
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
September 25, 1956-December 27, 1956
OOR Project No. 1452
Contract No. DA-01-009-ORD-431

Gentlemen:

Status Report No. 5 described an equation for correlating the relative reactivities of haloforms toward basic hydrolysis involving a divalent carbon intermediate. In order to make possible an adequate test of this equation, we have determined additional rate constants for the basic hydrolysis of haloforms (including some not studied previously) in water and in aqueous dioxane and for the base-catalyzed deuterium exchange of some new deuterohaloforms in aqueous solution. The equation appears to fit the new data about as well as it did the more limited data that originally suggested the correlation.

Mr. Stanton Ehrenson, who has been investigating this problem, should finish his research and write his Ph.D. thesis during the coming quarter.

Respectfully submitted,

[redacted]

Jack Hine
Project Director

Approved:

[redacted]

Wyatt C. Whitley, Chief
Chemical Sciences Division

JH/JJ
A-239

A-239

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

March 25, 1957

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 7, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
December 28, 1956 to March 25, 1957
OOR Project No. 1452
Contract No. DA-01-009-ORD-431

Gentlemen:

Mr. Stanton J. Ehrenson, Research Assistant on this project, has completed his research and written his Ph.D. thesis during the past quarter. His position has been filled by Mr. Donald C. Duffey who received his M.S. from the Rice Institute and is working toward a Ph.D. in organic chemistry at Georgia Tech.

Mr. Ehrenson's final correlations (see Status Report No. 5) of the relative reactivities of haloforms toward basic decomposition gave satisfactory results for data obtained in purely aqueous solution. However, iodoform reacted to fast to fit the correlation in aqueous dioxane, and bromoform reacted too fast in methanol. We have now found, though, that these deviations are due to the incursion of a free radical process, since the two reactions that deviate go much more slowly when diphenylamine is added to the reaction solution. We hope to get final data for the correlation equation during the current quarter.

Respectfully submitted:

[redacted]

Jack Hine
Project Director

Approved:

[redacted]

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

June 24, 1957

Commanding Officer
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2127 Myrtle Drive
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Subject: Status Report No. 8, Project No. A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute, March 26 to June 21, 1957
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

The work on an equation to correlate the relative reactivities of haloforms toward basic hydrolysis referred to in Status Reports 5, 6 and 7 has now been completed. A manuscript on this work, containing the first quantitative data on the effect of the structure of methylenes on their ease of formation, is being prepared and a copy will be submitted, probably during the next quarter.

During the last quarter we sent to the OOR a copy of a manuscript on "The Concerted Mechanism for α-Elimination of Haloforms" that we had submitted to the Journal of the American Chemical Society. In order to learn more about this "concerted mechanism" Mr. Donald Duffey had already begun an investigation of the decarboxylation of chlorodifluoroacetic acid. He is extending the investigation in his current work under this contract. During the last quarter he worked out a method for the determination of oxalate in the presence of chloride, fluoride, formate, acetate and chlorodifluoroacetate. Use of this method has shown that the decarboxylation reaction gives oxalate in addition to the previously observed products. The investigation of the mechanism of the decarboxylation of the chlorodifluoroacetate ion will continue during the next quarter.

Respectfully submitted,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA. GEORGIA

September 26, 1957

Commanding Officer
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2127 Myrtle Drive
Duke Station, Box CM
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Subject: Status Report No. 9, Project No. A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute, June 22 to September 25, 1957
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

The study of the decarboxylation of chlorodifluoroacetic acid referred to in Status Report No. 8 is now largely completed. From the result we conclude that the reaction is largely a concerted decompostion of the chlorodifluoroacetate ion to carbon dioxide, chloride ion, and difluoromethylene. In purely aqueous solution the difluoromethylene reacts further to give carbon monoxide or formic acid but in the presence of fluoride, chloride, bromide or iodide ions it may give $CHF_3$, $CHF_2Cl$, $CHF_2Br$, or $CHF_2I$. In a competing reaction, a smaller amount of the chlorodifluoroacetic acid is hydrolyzed to oxalic acid. We are currently preparing a manusript describing this work for submission to the Journal of the American Chemical Society.

Respectfully submitted:

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

A-239

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

January 8, 1958

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 10, Project No. A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute, September 26 to December 25, 1957
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the past quarter the preparation of a first draft of a manuscript on the decarboxylation of chlorodifluoroacetic acid revealed loopholes in some of the arguments and for this reason additional work has continued on this problem. We have now analyzed some of the reaction solutions directly for formate and shown that considerable amounts of formate are produced. This involved showing that chloride, fluoride, oxalate, acetate and chlorodifluoroacetate do not interfere with the analytical method. We have also proved that certain side reactions occur. For example, fluoride ions attack chlorodifluoroacetate to give trifluoroacetate ions. Rather surprisingly this reaction occurs even faster than the analogous reaction with the usually more nucleophilic bromide ions. This observation and our discovery that fluoride ions are usually reactive toward difluoromethylene suggests that fluoride ions may, in general, be more reactive than might have been expected toward carbon atoms that already bear fluorine substituents.

In addition to this work we have also studied the reaction of dibromofluoromethane with potassium isopropoxide. Certain other work had suggested that evidence for the formation of the reactive compounds i-PrOCHFBr or $(i\text{-PrO})_2CHF$ might thereby be obtained. In our investigation no such evidence was obtained, however.

Respectfully submitted:

[redacted]

Jack Hine
Project Director

Approved:

[redacted]

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA. GEORGIA

March 4, 1958

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 11, Project No. A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
December 26, 1957 to February 28, 1958
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the past quarter we have continued work on the mechanism of the decarboxylation of chlorodifluoroacetic acid. The analytical procedures for chloride, fluoride, oxalate, acetate, chlorodifluoroacetate, formate, haloforms, and trifluoroacetate that we have worked out previously have now been applied to the reaction in several runs and we have accounted for practically all of the reactant on the basis of these products.

We hope to finish this phase of the project during the current quarter and to send a manuscript describing the work to the Journal of the American Chemical Society. Simultaneously, of course, a copy of the manuscript will be submitted to the OOR. During the last quarter Technical Report No. 2, "Methylene Derivatives as Intermediates in Polar Reaction. IX. The Concerted Mechanism for $\alpha$-Elimination of Haloforms", was submitted.

Yours very truly,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

June 24, 1958

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 12, Project No. A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
March 1, 1958 - June 20, 1958
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the past quarter we have started work on attempting to generate alkoxyhalomethylenes by the action of base on $ROCHCl_2$ compounds. The preparation of $C_2H_5OCHCl_2$ from $PCl_5$ and $HCO_2C_2H_5$ described briefly in the literature was found to be made inconvenient by the fact that the product boils at almost exactly the same temperature as the by product, $POCl_3$.

An analogous preparation of $CH_3OCHCl_2$ from $HCO_2CH_3$ appears to have been successful, however. The product obtained has essentially the same physical properties as material described in the literature (prepared in poor yield by chlorination of $CH_3OCH_2Cl$). The $CH_3OCHCl_2$ reacts quite rapidly with base even in such poorly ionizing solvents as isopropyl alcohol.

We have not yet been able to determine, however, whether the rate of this reaction is proportional to the base concentration, or whether the reaction may be $Sn^1$ in character. We plan to approach a solution to this part of the problem by the use of lower temperatures and/or poorer ion-solvating media.

Yours very truly,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

September 26, 1958

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 13, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
June 20, 1958 - September 20, 1958
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

As stated in the last report we have been interested in the generation of alkoxyhalomethylenes, and have synthesized $CH_3OCHCl_2$ for use in this connection. Preliminary studies of the reaction of this compound with potassium isopropoxide suggest that methoxychloromethylene ($CH_3OCCl$) is indeed an intermediate.

The kinetics of the reaction in 75% benzene - 25% isopropyl alcohol at 0° show that the $CH_3OCHCl_2$ undergoes solvolysis by simultaneous first-order and second-order paths. In the presence of reasonable concentrations of potassium isopropoxide, however, the second-order path may be made to constitute more than 95% of the reaction. The rough second-order rate constant obtained is considerably larger than the value reported by other workers for the reaction of $CH_3OCH_2Cl$ with NaOEt in the somewhat similar solvent, 90% ether - 10% ethanol. This makes it seem improbable that the $CH_3OCHCl_2$ is reacting by the $S_N2$ mechanism since there is considerable evidence that $\alpha$-chlorine substituents decrease reactivity by the $S_N2$ mechanism. It therefore seems more likely that the reaction is initiated by an $\alpha$-dehydrochlorination.

$$i\text{-}PrO^- + CH_3OCHCl_2 \longrightarrow i\text{-}PrOH + CH_3OCCl + Cl^-$$

Perhaps even stronger evidence for this point of view is found in the fact that

carbon monoxide is a product of the reaction. Such a product could be explained by the reaction

$$i\text{-}PrO^- + CH_3OCCl \longrightarrow i\text{-}PrOCH_3 + CO + Cl^-$$

but would not seem very plausible as a product of an $S_N2$ reaction, which might be expected to yield an orthoester.

We plan to continue work on the kinetics and products of this reaction during the coming quarter.

Yours very truly

Jack Hine
Project Director

JH:bb

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA. GEORGIA

December 29, 1958

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 14, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
September 21, 1958 - December 23, 1958
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the current quarter we have continued our studies on $CH_3OCHCl_2$ since it seems possible that this compound will react with strong bases to give methoxychloromethylene ($CH_3OCCl$) as an intermediate.

The products of the reaction of $CH_3OCHCl_2$ with potassium isopropoxide have been investigated. In addition to about 0.6% of carbon monoxide and a like amount of methyl isopropyl ether, some methyl formate is produced as well as about 40% of a product that is believed to be $(i\text{-PrO})_2CHOCH_3$.

The reaction of $CH_3OCHCl_2$ with potassium t-butoxide in the presence of cyclohexene has also been studied, in the hope that $CH_3OCCl$ would be generated and combine with the olefin as other methylene intermediates are known to do. This reaction yielded a complex mixture of products that has been separated into a number of fractions. None of the fractions, except those consisting of an unreacted starting material, has yet been identified, however.

Yours very truly,

Jack Hine
Project Director

JH/ee

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

April 7, 1959

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 15, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
December 24, 1958 - March 31, 1959
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

With the end of the current quarter Mr. Donald C. Duffey completes his work as graduate research assistant on this project. His successor is to be Mr. John J. Porter, who is working toward the Ph.D. in organic chemistry at Georgia Tech and who has passed the qualifying exams for the Ph.D. Two papers describing Mr. Duffey's work on this project on the decarboxylation of dichlorofluoroacetic acid and chlorodifluoroacetic acid have just been published in the March 5 issue of the Journal of the American Chemical Society. When reprints of these papers are received they will be distributed as Technical Reports on the project.

Our work on the reactions of methyl dichloromethyl ether with bases has continued. The reaction with potassium t-butoxide in the presence of cyclohexene has been studied further but we were not able to isolate any new products from the reaction. The reaction of chloroform with sodium methoxide has been studied and found to yield

only a few per cent of carbon monoxide. The isolation of ethers in the reaction of other alkoxides with chloroform suggests that the carbon monoxide is formed by a nucleophilic substitution reaction. The fact that the yield of carbon monoxide is so low with methanol shows that the substitution reaction mechanism cannot be Sn2 but must be Sn1 for the other alcohols at least.

Respectfully submitted,

Jack Hine
Project Director

JH:jp

A-239

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

June 24, 1959

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 16, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
April 1, 1959 - June 23, 1959
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the current quarter, Mr. John J. Porter, the new graduate research assistant on the project, has directed his attention toward new methods for generating methylene intermediates from organic reactants other than haloforms. We are currently studying the reaction of $C_6H_5SO_2CHF_2$ with sodium methoxide in methanol solution. Preliminary investigations show that the reaction proceeds at a reasonable rate at 35-50°. From this observation it seems unlikely that the reaction is a simple bimolecular nucleophilic displacement ($S_N2$). In the first place, neither ordinary saturated organic fluorides nor sulfones react with base at significant rates at temperatures below about 100°. Furthermore, in all of the cases that appear to have been studied, both α-fluoro and α-benzenesulfonyl groups have been found to decrease $S_N2$ reactivity. Thus $C_6H_5SO_2CHF_2$ reacts with base much faster than it would be expected to react by the $S_N2$ mechanism. An $S_N1$ reaction mechanism, of course, is completely implausible. It therefore seems likely that the reaction proceeds by some mechanism involving a methylene intermediate, e.g.

$$C_6H_5SO_2CHF_2 + MeO^- \rightleftharpoons C_6H_5SO_2\overset{\ominus}{C}F_2 + MeOH$$

$$C_6H_5SO_2\overset{\ominus}{C}F_2 \longrightarrow C_6H_5SO_2^- + CF_2$$

Attempts to capture the $CF_2$ intermediates by the use of sodium thiophenylate were made, but the results were shown to be indecisive when it was found that benzenesulfinate ions interfere in the iodometric titration used in the analysis for sodium thiophenylate. We are now investigating the nature of this interference and hoping to develop a method for titrating thiophenol in the presence of benzenesulfinic acid.

Respectfully submitted,

Jack Hine
Project Director

APPROVED:

Wyatt C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

September 25, 1959

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 17, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
June 24, 1959 - September 24, 1959
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the current quarter, studies have shown that the addition of sodium methoxide increases the rate of reaction of sodium thiophenoxide with phenyl difluoromethyl sulfone. It therefore seems established that a methylene intermediate is formed in this reaction. We hope to get additional information by isolating the products of reaction of the sulfone with sodium methoxide alone, and with sodium methoxide in the presence of sodium thiophenoxide.

In connection with previous work, we have also checked the reactivity of methyl difluoromethyl sulfide toward sodium methoxide in methanol at 50°. We found very little reaction even after more than three weeks time. This observation shows that the trimethylorthothioformate that we have observed in the reaction of sodium thiomethoxide with chlorodifluoromethane in the presence of sodium methoxide could not have been formed by the further reaction of the methyl difluoromethyl sulfide also produced. Since all of the other plausible paths for the formation of the trimethylorthothioformate involve the intermediate, $CH_3SCF$, it follows that this methylene derivative must have been an intermediate in the reaction.

Respectfully submitted,

Jack Hine
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

December 28, 1959

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 18, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
September 25, 1959 - December 22, 1959
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

In the process of preparing a manuscript describing the evidence that $CH_3S-C-F$ is formed as an intermediate in the reaction of chlorodifluoromethane with sodium thiomethylate and sodium methoxide in methanol it was noted that data on the basicity of the thiomethylate ion at various ionic strengths was inadequate. For this reason we have determined the indicator constant for thymol blue at several ionic strengths and then used this indicator to determine the basicity constant of the thiomethylate ion in methanol at several ionic strengths up to 0.5 M.

In the study of the mechanism of the reaction of phenyl difluoromethyl sulfone with sodium methoxide in methanol we have confirmed our previous observation that the presence of sodium methoxide accelerates the reaction of sodium thiophenolate with the sulfone. These observations seem to show that the reaction involves the initial formation of a carbanion, which is in equilibrium with the reactants and which may, in the rate-controlling step of the reaction lose an anion to give a methylene intermediate. Although the anion being lost might be either the fluoride ion or the benzenesulfinate ion, the latter possibility seemed more likely in view of the ease of formation of the intermediate difluoromethylene established earlier in the work of this project. We are now carrying out product isolation studies that should enable us to decide definitely between the two alternatives. While this work is not yet complete we have isolated benzene-sulfinic acid, formed as its salt during the reaction, and this strengthens the argument that it is the benzenesulfinate ion rather than the fluoride ion that is lost by the carbanion in the rate controlling step of the reaction.

Respectfully submitted,

Jack Hine
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

**GEORGIA INSTITUTE OF TECHNOLOGY**
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

March 31, 1960

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 19, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
December 23, 1959 - March 28, 1960
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the current quarter a manuscript has been prepared describing the evidence that $CH_3S$-C-F is an intermediate in the reaction of sodium thiomethoxide with chlorodifluoromethane in the presence of sodium methoxide to give trimethylorthothioformate. When this manuscript has been reproduced, it will be submitted for publication in the Journal of the American Chemical Society and copies sent to the Office of Ordnance Research for approval.

In our study of the reaction of difluoromethyl phenyl sulfone with sodium methoxide, we have established the following mechanism for that part of the reaction up to and including the rate controlling step

$$C_6H_5SO_2CHF_2 + CH_3O^- \rightleftarrows C_6H_5SO_2CF_2^- + CH_3OH$$

$$C_6H_5SO_2CF_2^- \rightarrow CF_2 + C_6H_5SO_2^-$$

The difluoromethylene intermediate has been captured by methanol to give difluoromethyl methyl ether (in 38% yield) and by sodium thiophenoxide to give difluoromethyl phenyl sulfide (in 22% yield). In the reaction with sodium thiophenoxide the difluoromethyl methyl sulfide cannot have been formed by $S_N2$ attack on the sulfone to displace the benzenesulfinate anion since the sulfone reacts with sodium thiophenoxide in methanol at an appreciable rate only if sodium methoxide is present as a catalyst. We have observed that the sulfone undergoes reversible base-catalyzed deuterium exchange, showing that the difluoromethylene is formed by a step-wise process involving an intermediate carbanion as shown in the mechanism above, and not by a concerted one-step $\alpha$-elimination like that that appears to operate in the reaction of chlorodifluoromethane with bases. We are now studying the kinetics of this deuterium exchange process.

Respectfully submitted,

Jack Hine
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

This page has been redacted.

**GEORGIA INSTITUTE OF TECHNOLOGY**
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
September 30, 1960

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 21, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
~~March 29, 1960 - June 24, 1960~~ June 25, 1960 - Sept. 25, 1960
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

Mr. Gary G. Hammer has been chosen as the new research assistant on this project. Mr. Hammer is a candidate for the Ph.D. in organic chemistry at Georgia Tech and has passed the comprehensive examinations for this degree.

In a number of cases divalent carbon intermediates have been formed by the $\alpha$-elimination of HX from an organic molecule by the action of a strong base. Some of these reactions involve the intermediate formation of a carbanion

$$R\text{-}\overset{H}{\overset{|}{C}}\text{-}X + B^- \rightleftharpoons R\text{-}\overset{\ominus}{\overset{|}{C}}\text{-}X \rightarrow R\text{-}\overset{}{\overset{|}{C}}\text{-}R$$
$$\qquad\quad R \qquad\qquad\quad R \qquad\qquad\quad X^-$$

and even in some concerted $\alpha$-eliminations the transition state appears to have considerable carbanion character. For this reason Mr. Hammer is investigating the effect of structure on the stability of carbanions. It is planned to determine equilibrium constants for reactions of the type

$$RH + KNH_2 \rightleftharpoons RK + NH_3$$

by spectral measurements in $NH_3$ solution. We have constructed an appropriate spectral cell with double walls and a vacuum jacket to prevent "sweating" and "frosting" and with a self contained dry ice-cooled reflux condenser to keep the liquid ammonia from producing excessive pressure in the apparatus. Only preliminary measurements have been made at this date though.

Also during the current quarter a manuscript, "The Formation of Difluoromethylene from Difluoromethyl Phenyl Sulfone and Sodium Methoxide" was submitted to the OOR for approval and to the Journal of the American Chemical Society for publication.

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

Respectfully submitted,

Jack Hine
Project Director

**GEORGIA INSTITUTE OF TECHNOLOGY**
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

December 30, 1960

Commanding Officer
Office of Ordnance Research
2127 Myrtle Drive
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 22, Project A-239
Divalent Carbon Derivatives as Reaction Intermediates
Georgia Tech Research Institute
September 26, 1960 - December 26, 1960
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

Most of the past quarter has been spent in working with the high-vacuum system being used in connection with the experiments described in Status Report No. 21. The apparatus seems to be reasonably leakfree now and much has been learned about the proper method of preparation of a platinum catalyst for the reaction of potassium with ammonia to give potassium amide. In addition, the following compounds have been prepared:

$$CH_2(SCH_3)_2,\ CH_3CH_2CH_2CH(SCH_3)_2,\ \text{and}\ C_6H_5CH(SCH_3)_2.$$

All of these compounds have weakly acidic hydrogen atoms. It is thought that they may be capable of reacting with potassium amide to give carbanions that will subsequently lose $RS^-$ to give a divalent-carbon intermediate.

Respectfully submitted,

Jack Hine
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

**GEORGIA INSTITUTE OF TECHNOLOGY**
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

March 31, 1961

S. Army Research Office (DURHAM)
ke Station, Box CM
rham, North Carolina

bject: Status Report No. 23, Project A-239
"Divalent Carbon Derivatives as Reaction Intermediates"
Georgia Tech Research Institute
December 27, 1960 - March 29, 1961
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

ntlemen:

We have observed that $CH_2(SCH_3)_2$ reacts with potassium amide in liquid nonia to form a relatively stable salt, which may be alkylated by use of alkyl halide. When $CH_2(SCH_3)_2$ is treated with potassium amide in liquid nonia and then with n-propyl bromide, $n\text{-}C_3H_7CH(SCH_3)_2$ is formed in good eld.

$$CH_2(SCH_3)_2 + NH_2^- \rightarrow {}^{\ominus}CH(SCH_3)_2 \xrightarrow{n\text{-}C_3H_7Br} n\text{-}C_3H_7CH(SCH_3)_2$$

e stability of the salt was shown by the fact that the alkylation product n still be obtained in good yield even if the salt is permitted to stand l day in refluxing liquid ammonia before the propyl bromide is added.

The fact that this carbanion does not decompose under the reaction conditions to yield $CH_3S\text{-}C\text{-}H$ and $CH_3S^-$ is probably due in part to the relative stability of the methylene ($CH_3S\text{-}C\text{-}H$) and in part to the difficulty of displacing a $CH_3S^-$ anion from an organic molecule. During the next quarter we an to make additional studies on $CH_2(SCH_3)_2$.

Respectfully submitted:

Jack Hine
Project Director

PROVED:

rt C. Whitley, Chief
emical Sciences Division

**GEORGIA INSTITUTE OF TECHNOLOGY**
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

June 26, 1961

U. S. Army Research Office (DURHAM)
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 24, Project A-239
"Divalent Carbon Derivatives as Reaction Intermediates"
Georgia Tech Research Institute
March 30, 1961 - June 22, 1961
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

We have observed that upon reaction with potassium amide in liquid ammonia, $CH(SC_2H_5)_3$ gives a green carbanion with the structure $(C_2H_5S)_3C^-$. Although this observation would be expected in view of the analogous behaviour of $CH_2(SCH_3)_2$ reported in the last status report, the subsequent behaviour of the carbanion is different. Upon standing for several hours the green color faded and tetraethylthioethylene was isolated from the reaction mixture. We believe that this observation constitutes evidence that diethylthiomethylene was formed as an intermediate as shown in the following reaction mechanism.

$$(C_2H_5S)_3CH \xrightarrow{NH_2^-} (C_2H_5S)_3C^- \rightarrow C_2H_5S\text{-}C\text{-}SC_2H_5 + C_2H_5S^-$$

$$(C_2H_5S)_3C^- + (C_2H_5S)_2C \rightarrow (C_2H_5S)_3C\text{-}\bar{C}(SC_2H_5)_2$$

$$\downarrow$$

$$C_2H_5S^- + (C_2H_5S)_2C{=}C(SC_2H_5)_2$$

During the next quarter we plan additional studies on this reaction.

Respectfully submitted,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

**GEORGIA INSTITUTE OF TECHNOLOGY**
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

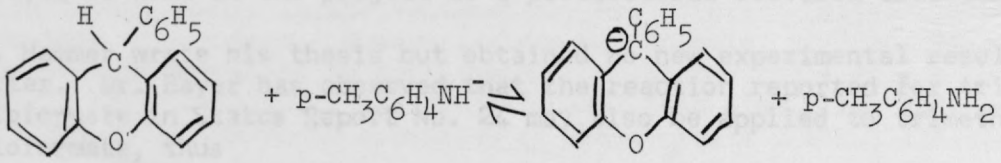
September 27, 1961

U. S. Army Research Office (DURHAM)
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 25, Project A-239
"Divalent Carbon Derivatives as Reaction Intermediates"
Georgia Tech Research Institute
June 23, 1961 - September 27, 1961
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

The measurement of the strengths of very weak acids referred to in Status Report No. 21 has been continued and the acidity of 9-phenylxanthane has been compared with that of p-toluidine.




In a first experiment a value of 0.15 has been obtained for K for the above equilibrium in liquid ammonia solution. The measurements were made by spectrophotometric determinations of the concentration of the highly colored 9-phenylxanthide anion.

Respectfully submitted,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

**GEORGIA INSTITUTE OF TECHNOLOGY**
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

December 22, 1961

U. S. Army Research Office (DURHAM)
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 26, Project A-239
"Divalent Carbon Derivatives as Reaction Intermediates"
Georgia Tech Research Institute
September 28, 1961 - December 22, 1961
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the current quarter Gary G. Hammer completed the work for his Ph.D. in organic chemistry at Georgia Tech and was terminated as the research assistant on this project. It was found impossible to secure a graduate student for the position during the last eight months of the project. Therefore, after doing without a research assistant for the month of November, Dr. Raymond P. Bayer was employed to work on the project as a postdoctoral research assistant.

Mr. Hammer wrote his thesis but obtained no new experimental results during the quarter. Dr. Bayer has observed that the reaction reported for triethyl orthothioformate in Status Report No. 24 may also be applied to trimethyl orthothioformate, thus

$$2(CH_3S)_3CH + 2KNH_2 \rightarrow (CH_3S)_2C{=}C(SCH_3)_2 + 2NH_3 + 2KSCH_3$$

Under the same reaction conditions the corresponding oxygen compound, trimethyl orthoformate, does not react.

During the coming quarter we plan to study the mono- and di-thio compounds, $CH_3SCH(OCH_3)_2$ and $(CH_3S)_2CHOCH_3$, and to try to obtain more direct evidence for the intermediacy of the carbanion, $(CH_3S)_3C^-$, in the reaction of the tri-thio compounds.

Respectfully submitted,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

March 26, 1962

U. S. Army Research Office (DURHAM)
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 27, Project A-239
"Divalent Carbon Derivatives as Reaction Intermediates"
Georgia Tech Research Institute
December 23, 1961 - March 26, 1962
OOR Project No. 1452, Contract No. DA-01-009-ORD-431

Gentlemen:

During the current quarter Dr. Raymond P. Bayer completed his post-doctoral work at Georgia Tech and was terminated as the research assistant on this project. Funds for approximately two months support for a Graduate Research Assistant remain in the contract and Mr. Robert McDaniel has been chosen for this appointment. However, since Mr. McDaniel will continue to work as a Teaching Assistant in the School of Chemistry until June 1 he may not begin employment under the project until that time. For this reason we plan to request a one-month extension of the contract without additional funds.

Our technical progress during the current quarter was covered in the manuscript sent you earlier this month.

Respectfully submitted,

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

**GEORGIA INSTITUTE OF TECHNOLOGY**
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

July 5, 1962

U. S. Army Research Office (DURHAM)
Duke Station, Box CM
Durham, North Carolina

Subject: Status Report No. 28, Project A-239
"Divalent Carbon Derivatives as Reaction Intermediates"
Georgia Tech Research Institute
March 27, 1962 - June 30, 1962

Gentlemen:

No research was carried out under the contract this quarter until June, when Mr. Robert McDaniel began work on the project. Mr. McDaniel is beginning a study to check reports that certain reactions of p-nitrobenzyl compounds with strong bases proceed via intermediate methylenes, e.g.,

$$p\ O_2NC_6H_4CH_2Cl \rightarrow p\ O_2NC_6H_4CH{=}CHC_6H_4NO_2\ p$$

After the termination of this contract at the end of July a final report describing the results of this and all the other work completed will be submitted.

During the current quarter a Communication to the Editor of the Journal of the American Chemical Society describing work carried out earlier under this contract was published. Reprints of this Communication have now been received and are being distributed as technical reports.

Respectfully submitted,

Jack Hine JH
Project Director

Approved:

Frederick Bellinger, Chief
Chemical Sciences and Materials
Division

A-239

GEORGIA INSTITUTE OF TECHNOLOGY

Department of Army Project No. 5B99-01-004

Ordnance R & D Project No. TB2-0001

OOR Project No. 1452

Technical Report No. 1

# DIVALENT CARBON DERIVATIVES AS REACTION INTERMEDIATES

Contract No. DA-01-009-ORD-431

by Jack Hine, N. W. Burske, Mildred Hine

and P. B. Langford

[Reprinted from the Journal of the American Chemical Society, **79**, 1406 (1957).]

# The Relative Rates of Formation of Carbanions by Haloforms

By Jack Hine, Norbert W. Burske, Mildred Hine and Paul B. Langford

[Reprinted from the Journal of the American Chemical Society, **79**, 1406 (1957).]


[Contribution from the School of Chemistry of the Georgia Institute of Technology]

# The Relative Rates of Formation of Carbanions by Haloforms[1]

By Jack Hine, Norbert W. Burske, Mildred Hine and Paul B. Langford

Received October 15, 1956

The effect of structure on reactivity in carbanion formation of haloforms was studied by measurements of the rates of hydroxide ion catalyzed transformation of deuterated bromoform, iodoform, dibromochloromethane, dichloroiodomethane and bromochlorofluoromethane to the corresponding protium compounds in homogeneous aqueous solution. Comparison of the resultant data with those known for other haloforms gives the reactivity series $CDI_3 \sim CDBr_3 > CDBr_2Cl > CDBrCl_2 \sim CDCl_2I > CDBr_2F > CDCl_3 > CDBrClF > CDCl_2F$ showing that $\alpha$-halogen substituents facilitate carbanion formation in the order I $\sim$ Br > Cl > F. The observed order is thought to be due to some combination of the inductive effect, polarizability and *d*-orbital resonance. The relative rates of carbanion formation from haloform are fairly well correlated with the rates of formation of the same carbanions by the decarboxylation of the corresponding trihaloacetic acids in the cases where quantitative data on the latter are available. The effect on reactivity of the replacement of one halogen by another decreases as the reactivity of the haloform in which the replacement is made increases. For bromochlorofluoromethane the rate constant for hydrolysis and the deuterium kinetic isotope effect were also obtained.

## Introduction

In order to learn more about the effect of structure on reactivity in carbanion formation as well as to investigate more thoroughly a mechanism for the basic hydrolysis of haloforms involving intermediate trihalomethyl anions[2] we have been studying

(1) Part VI in the series, "Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms." For Part V see ref. 4. Abstracted in part from the Ph.D. thesis of Norbert W. Burske, Georgia Institute of Technology, 1957.

(2) J. Hine, This Journal, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

the kinetics of the base-catalyzed deuterium exchange of haloforms.

Studies of chloroform[3] and dichlorofluoromethane[4] already have been described. The nearest other approach to a quantitative study of the relative rates of deuterium exchange of different haloforms appears to be due to Sherman and Bernstein.[5] These workers found that when 0.1 mole of chlorodibromomethane was shaken with 0.01 mole of sodium deuteroxide in 0.1 mole of deuterium oxide at 105° for four days the haloform isolated was 43% deuterated, while bromodichloromethane became only 16% deuterated under the same conditions. While these data suggest that the $\alpha$-bromo substituent increases reactivity in carbanion formations more than does $\alpha$-chlorine, this interpretation is complicated by the heterogeneous nature of the reaction and by the fact that the sodium deuteroxide catalyst was used up during the period of reaction. Since bromodichloromethane is known to hydrolyze more rapidly than chlorodibromomethane[6] it was probably subjected to the action of the alkaline catalyst for a shorter length of time. The necessity of kinetic studies in a homogeneous solution was pointed out.[5] We now report such studies in aqueous solution for bromodichloromethane, chlorodibromomethane, bromoform, dichloroiodomethane, iodoform and bromochlorofluoromethane.

## Results

For economic as well as other reasons we preferred to study carbanion formation of haloforms by measuring the rates of base-catalyzed deuterium exchange of *deutero*haloforms in "light" water solution. Our deuterohaloforms were prepared by three methods. Deuterodibromochloromethane and deuterobromoform, like deuterochloroform,[3] were prepared by the alkaline cleavage of the corresponding trihaloacetaldehyde in heavy water solution. Deuterodichloroiodomethane and deuteroiodoform, like deuterodichlorofluoromethane,[4] were prepared by the base-catalyzed deuterium exchange of the corresponding protium compounds with heavy water. Deuterobromochlorofluoromethane was prepared from deuterodibromochloromethane by the action of mercuric fluoride.

Kinetic measurements[7] show that for all of the haloforms we studied except bromochlorofluoromethane, the rate of alkaline hydrolysis is so small compared to the rate of base-catalyzed deuterium exchange that only a negligible amount of hydrolysis occurs during a kinetic run on deuterium exchange. Since the concentration of base therefore does not change during a kinetic run the reactions are all kinetically first order. Most of these haloforms were so reactive that it was not convenient to use standard sodium hydroxide as a catalyzing base, and therefore the reactions were run in ammonia–ammonium perchlorate buffers. As before, we have followed the kinetics by extracting the haloform from the aqueous solution with an organic solvent and determining the ratio of deuterohaloform to haloform concentration by infrared measurements.

We have assumed the reaction mechanism

$$CDX_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CX_3^- + HOD$$

$$CDX_3 + NH_3 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} CX_3^- + DNH_3^+$$

$$CHX_3 + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CX_3^- + H_2O$$

$$CX_3^- \xrightarrow{k_3} CX_2 + X^-$$

followed by rapid reactions of $CX_2$. We shall use the symbols $D = [CDX_3]_t$, $H = [CHX_3]_t$. $t$ = time (seconds), and $p_0 = D_0/(D_0 + H_0)$. An equation of the type employed previously[3]

$$k_1[OH^-] + k_a[NH_3] = \frac{2.303}{t} \log\left(p_0 + p_0 \frac{H}{D}\right) \quad (1)$$

may be used for these cases in which hydrolysis is much slower than deuterium exchange ($k_{-1}$ and $k_{-2} >> k_3$).

From a run using any given concentration of buffer a value of $k_1[OH^-] + k_a[NH_3]$ could be obtained and from several runs using different buffers (at constant ionic strength) values of $k_1$ and $k_a$ were calculated. These values for dichloroiodomethane, chlorodibromomethane and bromoform are listed in Table I. In all cases most of the reaction was due to hydroxide ion catalysis and the amount of reaction due to ammonia was so small that $k_a$ could not be determined at all accurately. In the case of iodoform the limited solubility of the haloform in water ($< 10^{-3}$ $M$) and its sensitivity to light and oxygen made our data much less dependable than those obtained with the other haloforms. Therefore, in calculating $k_1$ for iodoform we neglected the contributions of $k_a$, which could not have been very large, however.

TABLE I

RATE CONSTANTS FOR THE FORMATION OF CARBANIONS FROM HALOFORM BY HYDROXIDE IONS AND AMMONIA IN AQUEOUS SOLUTION

| Haloform | $10^2 k_1$, l. mole$^{-1}$ sec.$^{-1}$ 0.0° | 35.0° | $10^6 k_a$, l. mole$^{-1}$ sec.$^{-1}$ 0.0° | 35.0° |
|---|---|---|---|---|
| $CDClBr_2$ | 14.35 ± 0.20 | 1385 ± 47 | 0.8 ± 0.8 | 190 ± 190 |
| $CDBr_3$[a] | 57.9 ± 1.0 | 4660 ± 100 | 13 ± 10 | 1400 ± 1000 |
| $CDCl_2I$ | 2.75 ± 0.05 | 314 ± 7 | 0.4 ± 0.3 | 65 ± 55 |
| $CDI_3$ | 60.1 ± 3.1 | 1390 ± 80[b] | | |

[a] $k_1 = (832 \pm 20) \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ and $k_a = (200 \pm 200) \times 10^{-6}$ l. mole$^{-1}$ sec.$^{-1}$ at 19.9°. [b] At 24.5°.

In the case of bromochlorofluoromethane deuterium exchange was accompanied by a large amount of hydrolysis. It was therefore necessary to use the kinetic treatment employed previously for the similar case of dichlorofluoromethane.[4] In this connection it was necessary to determine $k_h$, the rate constant for hydrolysis [$k_h = k_2k_3/(k_{-2} + k_3)$]. Then values of the kinetic isotope effect, $k_1/k_2$, and of the individual rate constants, $k_1$ and $k_2$, could be determined. The results obtained are shown in Table II.

(3) J. Hine, R. C. Peek, Jr., and B. D. Oakes, THIS JOURNAL, **76**, 827 (1954).

(4) J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

(5) R. H. Sherman and R. B. Bernstein, *ibid.*, **73**, 1376 (1951).

(6) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956).

(7) Unpublished experiments, this Laboratory.

TABLE II

KINETIC DATA FOR HYDROLYSIS AND CARBONION FORMATION OF BROMOCHLOROFLUOROMETHANE

| | 0.0° | 15.0° | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|
| $10^4k_h$ | 13.2 ± 0.2 | 150 ± 5 | 24.8 ± 0.5 | 19.2 ± 2.0 |
| $10^4k_1$ | 21.0 ± .5 | 227 ± 5 | 24.3 ± .5 | 18.3 ± 2.0 |
| $10^4k_2$ | 36.5 ± .8 | 385 ± 9 | 24.1 ± .5 | 18.5 ± 2.0 |
| $k_1/k_2$ | 0.575 ± 0.007 | 0.590 ± 0.008 | | |

In Table III are summarized the values of $k_1$ at 0° for all the haloforms we have studied. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ also tabulated were, like those in Table II, calculated from the absolute rate equation.[8]

$$k = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

TABLE III

SUMMARY OF KINETIC DATA ON CARBANION FORMATION BY HALOFORMS IN AQUEOUS SOLUTION

| Haloform | $10^4k_1$ at 0.0° | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|
| $CDCl_2F$[a] | 0.893 ± 0.018 | 25.9 ± 0.6 | 17.7 ± 2.3 |
| CDBrClF | 21.0 ± .5 | 24.3 ± .5 | 18.3 ± 2.0 |
| $CDCl_3$[b] | 47.0 ± 1.0 | 23.5 ± .3 | 17.1 ± 1.5 |
| $CDBr_2F$[c] | 180 ± 10 | | |
| $CDCl_2I$ | 275 ± 5 | 22.1 ± .2 | 15.3 ± 1.0 |
| $CDBrCl_2$[d] | ~290 | | |
| $CDBr_2Cl$ | 1435 ± 20 | 21.3 ± .3 | 15.6 ± 1.0 |
| $CDBr_3$ | 5790 ± 100 | 20.3 ± .4 | 15.0 ± 1.5 |
| $CDI_3$ | 6010 ± 310 | 20.2 ± .8 | 14.5 ± 3.0 |

[a] Data from ref. 4. [b] Data from ref. 3. [c] Preliminary unpublished data by J. Hine and P. B. Langford. [d] Data from a single point, by R. C. Peek, Jr.

## Discussion

**Correlation with Decarboxylation Rates.**—From the data of Table III it may be seen that in haloforms the various halogens have the following relative abilities to increase reactivity in carbanion formation: I ~ Br > Cl > F. It is of interest to compare this order with that found in other carbanion formation reactions. Probably the most closely related available data are those on the decarboxylation rates of trihaloacetic acids. These decarboxylations are first order reactions of the carboxylate anions and very probably have the mechanism[9,10]

$$X_3CCO_2^- \longrightarrow CX_3^- + CO_2$$
$$CX_3^- + H_2O \longrightarrow CHX_3 + OH^-$$

with the first step rate controlling. The relative reactivities that have been reported, $Br_3CCO_2^-$[10] > $Br_2ClCCO_2^-$[11] > $Cl_3CCO_2^-$[9,10] > $BrClFCCO_2^-$[11] > $F_3CCO_2^-$,[12] are in qualitative agreement with our data. Furthermore our data provide a reasonable explanation for the difficulties that have been encountered in studying the kinetics of the decarboxylation of bromochlorofluoroacetic acid,[11] dichlorofluoroacetic acid[12] and chlorodifluoroacetic acid.[12] With these acids the decarboxylation reaction is accompanied by a considerable liberation of halide ions. This liberation of halide ions has been attributed both to hydrolysis of the acid occurring in competition with the decarboxylation and to hydrolysis of the haloform after decarboxylation.[11,12] However, our data show that the latter explanation is much more probable since the complication occurs with those acids whose corresponding haloforms hydrolyze at a rate comparable to their carbanion formation. In fact, the data in Table II show that 39% (150/385 = 0.39) of the bromochlorofluoromethyl carbanions formed at 15° under the conditions of our kinetic studies decompose without ever re-forming the haloform.

While only qualitative statements are made about the decarboxylation of dichlorofluoro- and difluorochloroacetic acids,[12] quantitative data were reported for bromochlorofluoroacetic acid.[11] The rate constants obtained for the decarboxylation (when followed by titration of the bicarbonate ion liberated by the reaction of the salt of the acid[11]) of acids of this type may tend to be too small, since the mineral acid liberated by hydrolysis will destroy the bicarbonate ion and will also transform some of the carboxylate anion into unreactive carboxylic acid. Hence the rate constant ($2.6 \times 10^{-6}$ l. mole$^{-1}$ sec.$^{-1}$) obtained by Sutherland and Aston[11] in the presence of 100% excess alkali is probably more reliable than the smaller value obtained with 10% excess alkali. Figure 1 is a log–log plot of the rate constants for carbanion formation by haloforms at 0° *versus* the rate constants for decarboxylation of the corresponding trihaloacetate anions at 70°.[13]

The deviations from complete linearity are probably significant and may be explained by assuming that the decarboxylation rates are influenced by steric factors. Pressure from the bulky halogen atoms may aid in expelling carbon dioxide from the carboxylate anion. The most convincing evidence for this point of view is the fact that triiodoacetic acid decarboxylates rather rapidly at room temperature and below[10,14] even though the triiodomethyl anion is not formed from the haloform significantly faster than is the tribromomethyl anion.

**Saturation Effect.**—While the replacement of a fluorine atom in a haloform by chlorine or a chlorine atom by bromine invariably increases the rate constant for carbanion formation, it does not do so by a constant factor. The effect produced by a given type of replacement consistently decreases with increasing reactivity of the haloform in which the replacement is made. This fact is shown graphically in Fig. 2 where the amount by which a given type of replacement increases log $k$ is plotted against log $k$ for replacements of fluorine

(8) S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(9) F. H. Verhoek, THIS JOURNAL, **56**, 571 (1934).

(10) R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

(11) L. H. Sutherland and J. G. Aston, THIS JOURNAL, **61**, 241 (1939).

(12) I. Auerbach, F. H. Verhoek and A. L. Henne, *ibid.*, **72**, 299 (1950).

(13) The rate constant for the tribromoacetate anion at 70° ($5.4 \times 10^{-4}$) attributed to Fairclough by Sutherland and Aston appears to be in error. We obtain the value $8.0 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$ from Fairclough's values of log $PZ$ and $E$. Although Moelwyn-Hughes and Johnson[14] obtained the constant $8.17 \times 10^{-4}$ for decarboxylation of tribromoacetic *acid*, the acid was apparently not entirely dissociated since the value $11.6 \times 10^{-4}$ is obtained by a 5.1° extrapolation of their data on the salt. We have plotted the value ($9.8 \pm 1.8$) $\times 10^{-4}$ for the tribromoacetate anion and as a rough estimate of the uncertainty used ($2.6 \pm 1.0$) $\times 10^{-6}$ for the bromochlorofluoroacetate anion.

(14) P. Johnson and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A175**, 118 (1940).

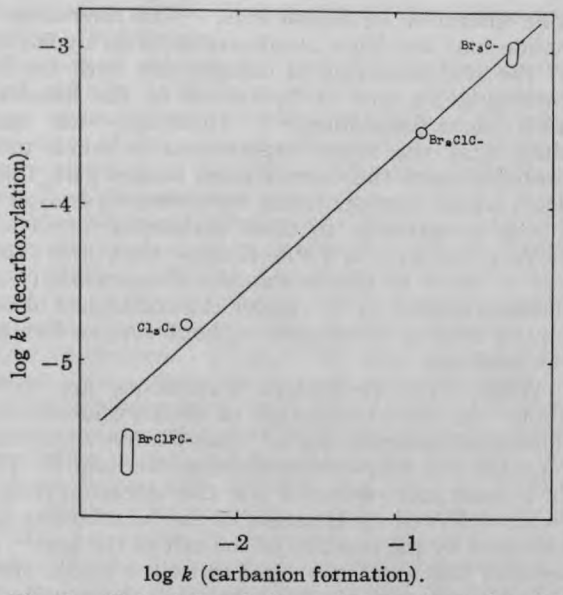



Fig. 1.—Plot of log $k$ for carbanion formation from deuterohaloforms at 0° *vs.* log $k$ for decarboxylation of corresponding trihaloacetate ions at 70°.

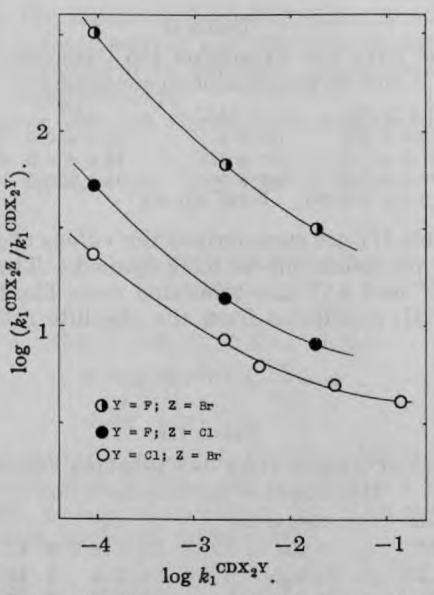



Fig. 2.—Plot of log $k_1$ for deuterohaloforms *vs.* the effect on log $k_1$ produced by replacing one halogen atom.

by chlorine, of chlorine by bromine and of fluorine by bromine. In the case of iodine only two rate constants are available but the same sort of relationship appears to hold. This observed diminishing effect upon successive replacement is a type of saturation effect. Branch and Calvin have discussed saturation effects in connection with their empirical equation for correlating the effect of structure on the ionization constants of fatty acid derivatives.[15]

The action of the halogen in facilitating carbanion formation may be viewed as one of lowering the free energy of the carbanion (and also of the transition state leading to it) by increasing the volume over which the negative charge is spread. Since the potential on a charged sphere is equal to the magnitude of the charge divided by the radius of the sphere, we might expect a somewhat hyperbolic plot in Fig. 2 even if the extent to which a given halogen distributed the negative charge on the adjacent carbon was constant. Actually it appears more probable that the extent to which any one halogen distributes the charge would depend somewhat on the extent to which the charge was already distributed by the other two halogens. In any case, the experimental curve appears to be of the general type that might be expected from theoretical considerations. In this connection the success of linear free energy relationships like the Brönsted catalysis law, the Hammett equation, Taft's equations, etc.,[16] is of interest. While such equations as usually applied do not neglect saturation effects, they do require them to be constant for the various reaction series compared. Perhaps saturation effects are particularly large in the present case because the changes in structure are being made so close to the center of reaction. Nevertheless the range of $10^4$ in our observed rate constants is no larger than that obtained in many other reactions. We believe that the impossibility of internal rotation in our compounds may have eliminated a factor that has complicated many other reactivity studies.

**Reasons for the Effect of Halogens on Reactivity.**—While the ease of carbanion formation of chloroform has been attributed to the electronegativity of the chlorine atoms, our data make it clear that other factors must also be of at least comparable importance. There appear to be three factors that might be considered in explaining why the effect of the $\alpha$-halogens on rates of carbanion formation is almost the reverse of that expected from the inductive effect. One factor is B-strain.[17] That is, there may be repulsions between the three halogen atoms of the tetrahedral haloform that are somewhat relieved upon formation of the more nearly planar carbanion. Steric effects should increase in size quite rapidly once they have become at all important. However the replacement of chlorine by bromine in our compounds produces a significant increase in reactivity. If this is due to B-strain counteracting the decrease in electronegativity (0.2 unit), then the replacement of bromine by iodine should increase the reactivity at least as much since the decrease in electronegativity (0.3 unit) is not much larger. Another argument against the importance of B-strain in the present instance relates to the effect of iodine compared to bromine in two cases. If the comparable reactivities of $CDCl_2I$ and $CDBrCl_2$ are due to an approximate equality of B-strain and the inductive effect, then the B-strain factor should be much more important in a comparison of $CDI_3$ and $CDBr_3$. The observation that the latter two haloforms are equally reactive, within experimental error, shows that B-strain should not be contributing more than about

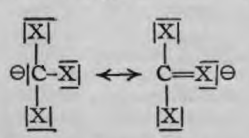
(15) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, sec. 25.

(16) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, secs. 8-1c, 2-4e, 12-3c.

(17) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944); H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

15% to the reactivity in this case. Its contribution should be less in all other cases.

A second factor that should be considered is "d-orbital resonance," by which trihalomethyl carbanions may be stabilized through the resonance contribution of structures having ten electrons in the outer shell of a halogen atom. Doering, Levy,



Schreiber and Hoffmann have attributed the greater ease of carbanion formation by sulfonium and phosphonium ions, in comparison to ammonium ions, to this factor.[18] In the present case the high energy that would be required to expand the outer electronic octet of fluorine may analogously explain why fluorine is the poorest of the halogens at facilitating $\alpha$-carbanion formation, despite its great electronegativity. Doering and Hoffmann found the orders S > Se > Te, and P > As > Sb > N for carbanion formation rates in polymethyl "onium" ions. They made crude calculations to show that the contribution of *d*-orbital resonance was roughly constant for the "onium" ions derived from second, third and fourth row elements, the observed differences in reactivity being due to coulombic effects.

Since decreasing electronegativity within a given family of the periodic table is associated with increasing covalent radius of the elements (and hence greater shielding of the nucleus) we might have expected the order Cl > Br > I > F if *d*-orbital resonance is important but constant for the three heavier halogens. However, because of the approximate character of Doering and Hoffmann's calculations, their neglect of polarizability effects and the fact that their experiments refer to different families in the periodic table, we do not feel safe in assuming that d-orbital resonance is essentially equally important for chlorine, bromine and iodine. We are not sure, however, how to assess the relative importance of this factor for these three halogens and it is possible that the differences in reactivity have their origin in d-orbital resonance.

The probable importance of a third factor, polarizability, however, seems too important to overlook. In fact, the interaction of polarizability and the inductive effect, seems to offer not too improbable an explanation of our entire reaction series, with the complete neglect of *d*-orbital resonance. Judging from atomic refractive constants, the largest change in polarizability in the halogen series occurs between fluorine (0.997) and chlorine (5.967) with much smaller percentage increases being found upon going to bromine (8.865) and iodine (13.900).[19] The importance of polarizability should be greater with haloforms than with "onium" ions, since although neutral halogens are probably individually slightly less polarizable than the corresponding positively charged atoms of group V and VI,[20] there are three halogens to be compared with only one positive group V or VI atom. It may be for this reason that the maximum activating influence for halogens in haloforms occurs in the third or fourth period while it occurs in the second period for "onium" ions.[18] In both cases it is difficult to assess the relative importance of polarizability and d-orbital resonance. Tiers has recently described evidence that closely located halogen atoms may give "apparent electron withdrawal" by what appears to be a steric effect.[21] This effect may be of importance with the haloforms.

From the data of Table III it is clear that the observed differences in reactivity are at least partially due to differences in heats of activation. The observed entropies of activation are all considerably positive. The attack of hydroxide ion on a haloform to give a trihalomethyl anion very probably involves the dispersal of the negative charge in the transition state over a larger volume than it occupied in the reacting hydroxide ion. Since this more diffuse charge should have a smaller orienting effect on surrounding solvent molecules it probably contributes to the positive entropy of activation. There must be other factors operating, too, though, since the activation entropies appear to decrease with increasing reactivity of the haloforms, although it is the more reactive haloforms for whose anions the negative charge should be more diffuse. The heats and entropies of activation follow reasonably well the relationship

$$\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \beta \Delta S^{\ddagger}$$

recently discussed by Leffler,[22] the correlation coefficient, $r$, being 0.921. A least squares treatment gave an iso-kinetic temperature $\beta$ = 1340°K. and $\Delta H_0^{\ddagger}$ = 0.75 kcal./mole.

In the only other direct comparison of the relative effects of two different halogens on ease of proton removal to form a carbanion of which we are aware, Bell and Lidwell found bromoacetone to undergo base-catalyzed iodination faster than chloroacetone.[23]

## Experimental

**Deuterohaloforms.**—Deuterodibromochloromethane was prepared from dibromochloroacetaldehyde.[24] From 104.6 g. (0.45 mole) of aldehyde and 50 g. of 99.6% deuterium oxide, in which 10.7 g. (0.47 mole) of metallic sodium had been dissolved by shaking with external cooling, was obtained a yellow organic layer that was washed with water and dried with silica gel. Fractional distillation over phosphorus pentoxide through a 50-cm. column gave 61 g. (66%) of material boiling at 117.1–117.6° at 737 mm., $n^{34}$D 1.5390.

Deuterobromoform was prepared analogously from bromal, and the material boiling at 92–93° at 135 mm. was used.

Deuterodichloroiodomethane was prepared by stirring dichloroiodomethane with alkaline heavy water in a low actinic flask under nitrogen at room temperature. From 15 ml. of the haloform, after stirring twice with 35% and once with 99.6% deuterium oxide, was obtained 10 ml. of deuterated haloform, $n^{32}$D 1.5790.

(18) W. von E. Doering and L. K. Levy, THIS JOURNAL, **77**, 509 (1955); W. von E. Doering and K. C. Schreiber, *ibid.*, **77**, 514 (1955); W. von E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955).

(19) Lange's "Handbook of Chemistry," 6th ed., Handbook Publishing Co., Sandusky, Ohio, p. 1025.

(20) *Cf.* data listed in C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Sec. 10-b.

(21) G. V. D. Tiers, THIS JOURNAL, **78**, 2914 (1956).

(22) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(23) R. P. Bell and O. M. Lidwell, *Proc. Roy. Soc.* (*London*), **A176**, 88 (1940).

(24) O. Jacobsen and A. Neumeister, *Ber.*, **15**, 600 (1882).

Deuteroiodoform was prepared similarly except that the alkaline heavy water was mixed with half its volume of dioxane to increase the solubility of the iodoform. After exchange the deuterated iodoform was recrystallized from slightly acidified methanol to give material, m.p. 118–120°.

Deuterobromochlorofluoromethane was prepared from 47.2 g. (0.23 mole) of deuterodibromochloromethane and 25 g. (0.11 mole) of mercuric fluoride by the method described previously for the protium analog.[25] The fraction, b.p. 35.8–36.2° (740 mm.), weighed 18.1 g. (53.7%), $n^{28}D$ 1.4133.

**Other Reagents and Apparatus.**—The preparation and purification of the haloforms used were carried out by the methods described earlier.[25] The temperature control for kinetic runs also has been described.[25] "Oxygen-free" water was prepared by boiling distilled water and cooling it under an atmosphere of nitrogen.

**Kinetic Runs.**—The exchange of deuterodibromochloromethane was studied by the following type of procedure. Into a nitrogen-filled low actinic 100-ml. volumetric flask was pipetted 80 ml. of oxygen-free water and 0.100 ml. of 0.1310 *N* perchloric acid (to ensure that no deuterium exchange took place before the buffer was added). About 0.07 ml. of 93.0% deuterodibromochloromethane was added by use of a 0.25-ml. tuberculin syringe and the flask was shaken violently for the considerable amount of time required to dissolve the haloforms. After the flask had reached thermal equilibrium in a constant temperature bath, 10 ml. of a buffer at the same temperature was added and the flask shaken to start the reaction. For one set of points a buffer 0.2499 *N* in $NH_3$ and 0.3965 *N* in $NH_4ClO_4$ was used and in another set 0.0962 *N* $NH_3$, 0.1547 *N* $NH_4ClO_4$, 0.24 *N* $NaClO_4$ was employed. The reaction was stopped by the addition of 10 ml. of 1.146 *N* $HClO_4$ and the resultant solution extracted with two 3-ml. portions of isoöctane. The combined isoöctane extracts were stored in a black flask until they were analyzed isotopically.

Deuterodichloroiodomethane was studied in essentially the same way except that about 0.08 ml. of 85.1% deuterodichloroiodomethane was used per point.

With deuterobromoform about 0.04 ml. of 99.4% pure material was dissolved in the oxygen-free water and only one 4-ml. portion of isoöctane was used for extraction.

The very slight solubility of iodoform in water necessitated a modification of the procedure for this compound. In a typical run, 4000 ml. of oxygen-free water and 40 ml. of 0.0531 *N* perchloric acid (to prevent exchange) was shaken for four hours with 0.2 g. of deuterated iodoform. The solution was then filtered and 1900 ml. placed in each of two 2-l. volumetric flasks in a constant temperature bath. At zero time 100 ml. of 0.1078 *N* $NH_3$, 0.1023 *N* $NH_4ClO_4$ was added to one flask and 100 ml. of 0.0431 *N* $NH_3$, 0.0409 *N* $NH_4ClO_4$, 0.0614 *N* $NaClO_4$ added to the other. Samples were taken at various times by pouring about 660 ml. of reaction mixture into about 32 ml. of 1.18 *N* perchloric acid and extracting with 4 ml. of carbon disulfide. A "zero point" was taken by infrared analysis of the carbon disulfide extract from a similar 660-ml. deuteroiodoform solution to which no buffer was added. All operations were carried out under nitrogen and, to as great an extent as feasible, in the dark. The rate constants calculated, ignoring catalysis by bases other than hydroxide ion, are shown with the other data obtained at 24.5° in Table IV. The fact that the rate constants obtained with the more concentrated buffer are no higher (they are lower, if anything) shows that no *major* part of the reaction was due to ammonia catalysis.

Bromochlorofluoromethane was studied by methods analogous to those used previously for dichlorofluoromethane.[4] For the hydrolysis kinetics about 0.08 ml. of haloform was weighed under nitrogen into each of several 100-ml. volumetric flasks containing 80 ml. of oxygen-free water. The reactions were started by adding standard base, stopped with standard acid and then titrated to the brom thymol blue endpoint with standard base. This end-point, at *p*H of about 7, was used instead of phenolphthalein to prevent the further interaction of the very reactive haloform with base.[26] The same type of procedure was followed for the deuterium exchange runs except that about 0.06 ml. of 96% deuterobromochlorofluoromethane was used, and when the titration was completed the solution was slightly acidified and extracted with two 3-ml. portions of isoöctane for isotopic analysis.

The kinetic isotope effect, $k_1/k_2$, was determined by use of the integrated form of the equation[4]

$$dy/dt = s_0(1 + my - ny^2)(B_0 - y)$$

where

$$s_0 = k_h(3 + f)[(k_1/k_2)D_0 + H_0]$$

$$y = B_0 - B$$

and $m$ and $n$ are constants chosen by the method of least squares to give the optimum agreement with the experimental data. Then values of $k_1$ (and hence $k_2$) were calculated from the equation[4]

$$\left(\frac{D_0}{D}\right)^{1-(k_h/k_1)} = \frac{[1 - (k_h/k_1)](H/D) - (k_h/k_2) + 1}{[1 - (k_h/k_1)](H_0/D_0) - (k_h/k_2) + 1}$$

The relevant data obtained at 0° are listed in Table V.

TABLE IV

KINETICS OF THE DEUTERIUM EXCHANGE OF $CDI_3$ IN AQUEOUS AMMONIA BUFFERS AT 24.5°

$\frac{[CDI_3]_0}{[CHI_3]_0 + [CDI_3]_0} = 0.557$ $[CHI_3] + [CDI_3] \sim 5 \times 10^{-4}$ *M*

| Time, sec. | $[CHI_3]/[CDI_3]$ | $10^4 k_1[OH^-]$ (liters mole$^{-1}$ seconds$^{-1}$) | $k_1$ |
|---|---|---|---|
| 1330[b] | 1.9555 | 3.749 | 14.5 |
| 1700[b] | 2.4738 | 3.883 | 15.0 |
| 1890[a] | 2.6739 | 3.790 | 13.8 |
| 2370[b] | 3.6575 | 4.023 | 15.6 |
| 2490[a] | 3.4864 | 3.679 | 13.4 |
| 2820[a] | 4.037 | 3.658 | 13.3 |
| 3060[b] | 4.449 | 3.627 | 14.0 |
| 4080[a] | 6.686 | 3.564 | 13.0 |
| 4560[b] | 6.990 | 3.275 | 12.7 |
| | | Av. | 13.9 ± 0.8 |

[a] $[NH_3] = 0.0534$, $[NH_4ClO_4] = 0.0517$. [b] $[NH_3] = 0.0210$, $[NH_4ClO_4] = 0.0210$, $[NaClO_4] = 0.0307$.

TABLE V

DEUTERIUM EXCHANGE OF BROMOCHLOROFLUOROMETHANE IN AQUEOUS SOLUTION AT 0°

$[OH^-]_0 = 0.01712$, $m = 4.7$, $n = 1734$, $D_0/(H_0 + D_0) = 0.9598$

| Time, sec. | $H_0 + D_0$ | $\Delta[OH^-]$ | $D/(H + D)$ | $k_1/k_2$ | $10^4 k_1$ |
|---|---|---|---|---|---|
| 4719 | 0.00905 | 0.00192 | 0.8646 | 0.5645 | 2.190 |
| 7542 | .00996 | .00323 | .8261 | .5621 | 2.125 |
| 9306 | .01200 | .00465 | .8034 | .5866 | 2.166 |
| 10991 | .00962 | .00439 | .7817 | .5759 | 2.110 |
| 16291 | .00896 | .00573 | .7282 | .5827 | 2.056 |
| 22717 | .00928 | .00758 | .6832 | .5777 | 2.025 |
| 27004 | .00967 | .00871 | .6575 | .5737 | 2.039 |
| | | | Av. | 0.5747 | 2.096 |

**Isotopic Analysis.**—Haloforms were analyzed for their extent of deuteration by infrared measurements as described previously. The following are wave lengths at which measurements were made and then apparent molecular extinction coefficients in the same order, first for the haloform listed and then for the corresponding deuterohaloform: $CHCl_2I$, 8.845, 11.117, 11.866 and 13.217 μ; 159 ± 2.1, 0.28 ± 0.01, −0.04 ± 0.01 and 343.1 ± 3.2; −1.7 ± 0.2, 153.9 ± 1.5, 282.1 ± 3.1 and −0.085 ± 0.01. $CHBr_2Cl$, 8.730, 11.263, 11.717 and 13.346 μ; 118.5 ± 1.5, −0.5 ± 0.1, −0.7 ± 0.1 and 299.3 ± 2.4; −0.63 ± 0.1, 177.5 ± 0.8, 234.2 ± 1.0 and 3.9 ± 0.4. CHBrClF, 9.399, 10.983, 12.882 and 13.491 μ; 433.3 ± 3.1, 0.0 ± 0.1, 504.6 ± 2.3 and 0 ± 0.1; 261.2 ± 2.0, 315.9 ± 2.6, −0.07 ± 0.1 and 255.3 ± 4.7. $CHBr_3$, 8.733, 11.576 and 11.802 μ; 241.5 ± 5, −0.15 ± 0.05 and −0.44 ± 0.1; −0.066 ± 0.01, 158.5 ± 2 and 235.4 ± 3. $CHI_3$, 9.447 and 12.760 μ;

(25) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., THIS JOURNAL, **78**, 479 (1956).

(26) We used the values for *f*, 0.629 at 0° and 0.625 at 15°, that had been determined previously by A. M. Dowell, Jr. (Ph.D. thesis, Georgia Institute of Technology, 1954).

160 ± 1 and 0 ± 0.1; 0 ± 0.1 and 305 ± 7. Extinction coefficients tabulated above for the deuterium compounds are for the pure materials. The figures were obtained from the data on the mixtures of deuterium and protium compounds actually used by assuming that the "pure" deuterium compound absorbed only negligibly at at least one of the maxima for the protium compound.[27] From this assumption the percentage of deuteration of the actual haloform sample was calculated as follows: $CDCl_2I$ 85.1%, $CDBr_2Cl$ 93.0%, CDBrClF 95.9%, $CDBr_3$ 99.4% and $CDI_3$ 55.7%. These values are minima and will be higher if the assumption is wrong. While the correctness of the assumption can influence the values of $k$ obtained with bromochlorofluoromethane, it is obvious that the assumption cannot be wrong by more than 4% in this case. Furthermore, if the assumption were seriously in error the values of $k$ should show a large drift with time. For those haloforms whose hydrolysis occurs at a rate negligible compared to that of the deuterium exchange, the following argument shows that the values of $k$ obtained are completely independent of the validity of the assumption that the pure deuterium compound does not absorb at the protium maximum. If the assumption is incorrect the calculated fraction of deuteration of haloform will be in error. Let us denote this calculated fraction as $p/r$, where $p$ is the true value. Since our values of $p/r$ and of $\epsilon^{CDX_3}$ are obtained from measurements on samples of known total haloform concentration $(H + D)$ they are related to the optical density as

(27) This means that the *apparent* extinction coefficient of the deutero compound is the negative of the *actual* extinction coefficient of the solvent.

$$\text{optical density} = l\left[\frac{p}{r}\epsilon^{CDX_3}(H + D) + \left(1 - \frac{p}{r}\right)\epsilon^{CHX_3}(H + D)\right]$$

The optical density may also be expressed in terms of $\epsilon^{CDX_3*}$, the *true* extinction coefficient for the deuterohaloform.

$$\text{optical density} = l\,[p\epsilon^{CDX_3*}(H + D) + (1 - p)\epsilon^{CHX_3}(H + D)]$$

Eliminating the optical density between these two equations and solving for $r$

$$r = \frac{\epsilon^{CDX_3} - \epsilon^{CHX_3}}{\epsilon^{CDX_3*} - \epsilon^{CHX_3}}$$

This shows that $r$, the ratio of the true fraction of deuteration to the value we used, is a constant, independent of the haloform concentration and of $p$. In equation 1 we have the term

$$\log\left(p_0 + p_0\frac{H}{D}\right)$$

which can be written $\log (p_0/p)$. Instead of this we have been using $\log (p_0/r)/(p/r)$ which is, of course, identical.

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# METHYLENE DERIVATIVES AS INTERMEDIATES IN POLAR REACTIONS. IX. THE CONCERTED MECHANISM FOR ALPHA-ELIMINATIONS OF HALOFORMS

Contract No. DA-01-009-ORD-431

by

Jack Hine and P. B. Langford

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# Methylene Derivatives as Intermediates in Polar Reactions. IX. The Concerted Mechanism for alpha-Eliminations of Haloforms

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

# Methylene Derivatives as Intermediates in Polar Reactions. IX. The Concerted Mechanism for $\alpha$-Eliminations of Haloforms[1]

BY JACK HINE AND PAUL B. LANGFORD

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The kinetics of the alkaline hydrolysis of bromodifluoromethane and chlorodifluoromethane have been studied in aqueous solution at 0° and 20 or 25°. The reactivities are much greater than would be expected for the $S_N2$ mechanism. For this reason and the fact that the $S_N2$ mechanism has already been disproved for the basic methanolysis of chlorodifluoromethane, it is believed that the hydrolysis of these two haloforms, like that of others studied previously, involves the formation of an intermediate dihalomethylene. However, the two haloforms now studied hydrolyze faster than they would be expected from extrapolation of data on other haloforms) to form carbanions. For this reason and the facts that $\alpha$-fluorine (compared to other halogens) appears to stabilize dihalomethylenes and to destabilize trihalomethyl anions, the basic hydrolysis of bromodifluoromethane and chlorodifluoromethane is thought to be initiated by a *concerted* $\alpha$-elimination, in contrast to the two-step process involving an intermediate carbanion that occurs with the haloforms studied previously. This mechanism is supported by the observation that the basic hydrolysis of deuterobromodifluoromethane, unlike that of all of the other deuterohaloforms that have been studied, is not accompanied by deuterium exchange.

## Introduction

It has been found that the reaction of chlorodifluoromethane with sodium methoxide in methanol,[2] like the basic hydrolysis of chloroform[3] and other haloforms,[4] involves the intermediate formation of a dihalomethylene. With non-fluorine containing haloforms such as chloroform and bromoform, the intermediate trihalomethyl anions in the scheme

$$CHX_3 + OH^- \rightleftharpoons CX_3^- + H_2O$$
$$CX_3^- \longrightarrow CX_2 + X^-$$

decompose to dihalomethylene only 0.1–0.001% of the times that they are formed in alkaline aqueous solution.[5] Thus the reaction involves a rapid reversible formation of carbanions followed by a rate-controlling decomposition of the carbanions. With haloforms such as dichlorofluoromethane,[6] bromochlorofluoromethane[5] and dibromofluoromethane[7] that contain one fluorine atom, the carbanion decomposition is still rate-controlling, but it now occurs 8–40% of the times that the carbanion is formed. It therefore seemed that with haloforms containing two fluorine atoms the carbanion formation might become the rate-controlling step of the reaction, with decomposition occurring essentially every time that the carbanion is formed. Thus, although the monofluoro compounds were more reactive than their unfluorinated analogs, the difluorinated compounds were expected to show a decrease in reactivity due to the effect of $\alpha$-fluorine (relative to other halogens) of decreasing rates of carbanion formation. We decided to test this possibility.

## Results and Discussion

**The High Reactivity of $CHBrF_2$ and $CHClF_2$.**—The halogen atoms of haloforms facilitate carbanion formation in the order I ~ Br > Cl > F, the magnitude of the change in rate produced by a given change in halogen atoms decreasing rather smoothly with the increasing reactivity of the haloform.[5] Hence when log $k^{CHX_2Y}$ is plotted against log $k^{CHX_2Z}$ for the three types of cases for which data are available, smooth curves are obtained. This is illustrated in Fig. 1 in which the eleven circular symbols that fall on the three curves were plotted from data on the seven haloforms, $CHCl_2F$, CHBrClF, $CHCl_3$, $CHBr_2F$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$.[8] The three of these circles that are solid, for example, have for their abscissas, log $k$'s for $CHCl_2F$, CHBrClF and $CHBr_2F$ and for their ordinates, values for $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$, in the same order.

The square symbols in Fig. 1, obtained by extrapolation[9] of the curves, may be used to calculate "predicted rate constants" for carbanion formation for bromodichloromethane and chlorodifluoromethane. These predicted rate constants should be maxima for the hydrolysis rate constants if the hydrolysis involves the intermediate formation of trihalomethyl anions. On determining the hydrolysis rate constants for bromodifluoromethane and chlorodifluoromethane, as listed in Table I, we were therefore surprised to find values at least forty times[9] as large as would be expected for carbanion formation.

TABLE I

KINETIC DATA FOR BASIC HYDROLYSIS IN AQUEOUS SOLUTION

| Haloform | $10^4k$ (l./mole sec.) 0.0° | 20.1° | $\Delta H^\ddagger$, kcal./mole | $\Delta S^\ddagger$, e.u. |
|---|---|---|---|---|
| $CHBrF_2$ | 20.8 ± 0.8 | 374 ± 10 | 22.3 ± 0.7 | 11.1 ± 2.5 |
| $CDBrF_2$ | 10.3 ± .5 | | | |
| $CHClF_2$ | 0.17 ± .01 | 8.0 ± 0.5[a] | 24.4 ± .8 | 9.0 ± 3 |

[a] At 25°.

Since the reaction appears to be too fast to involve carbanion formation, we considered the possi-

1) This work was supported in part by the Office of Ordnance Research, U. S. Army.

2) J. Hine and J. J. Porter, THIS JOURNAL, **79**, 5493 (1957).

3) J. Hine, *ibid.*, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

4) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956).

5) (a) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, 1406 (1957); (b) S. J. Ehrenson, Ph.D. Thesis, Georgia Institute of Technology, Atlanta, Georgia, 1957.

6) J. Hine and N. W. Burske, THIS JOURNAL, **78**, 3337 (1956).

7) Unpublished work from this Laboratory.

(8) To obtain values of $k^{CHX_3}$ from the observed $k^{CDX_3}$ values[5] for the five haloforms for which kinetic isotope effects were not determined directly, a value of 1.75 was chosen for $k^{CHX_3}/k^{CDX_3}$ by averaging the values for dichlorofluoromethane (1.76) and bromochlorofluoromethane (1.74). The preliminary value[5] of $k^{CDBr_2F}$ was replaced by a final value[7] ($2.07 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$).

(9) The extrapolation was done conservatively by tending to straighten the extrapolated portion of the curves. If the original curvatures were maintained, the deviations of predicted carbanion formation rate constants from observed hydrolysis rate constants would be much larger than forty fold, especially for chlorodifluoromethane.

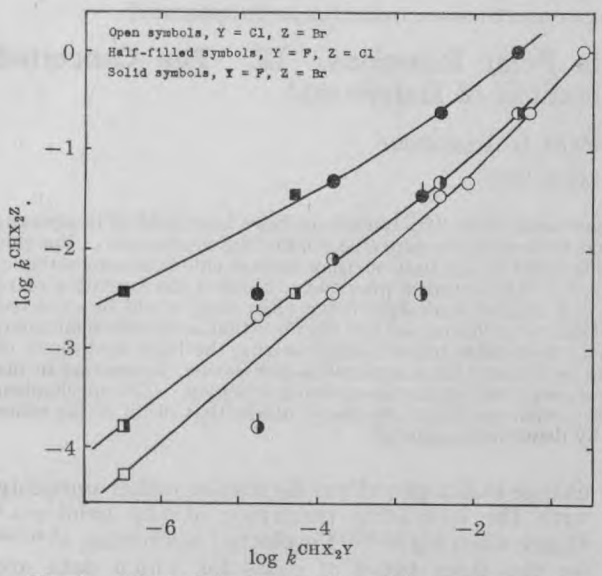


Fig. 1.—Effect of the change of one halogen atom on reactivity in the carbanion formation of haloforms. Symbols of the types, ●, ◐ and ○ were plotted from data on $CHClF_2$ and/or $CHBrF_2$. The square symbols are for values obtained by extrapolation.

bility that it might be occurring by the $S_N2$ mechanism. However, the data of Moelwyn-Hughes on the reactions of methyl chloride and methyl bromide with sodium hydroxide in aqueous solution[10] show that our difluoro derivatives of these compounds are 100 and 500 times as reactive at 25°. In view of the fact that α-fluorine has been shown to decrease $S_N2$ reactivity (compared to α-hydrogen),[11] it seems very improbable that the haloforms are reacting by the $S_N2$ mechanism. Further evidence may be found in the fact that the $S_N2$ mechanism has been disproved for the reaction of chlorodifluoromethane with sodium methoxide in methanol.[2] The fact that methyl bromide and iodide react faster with methanolic sodium methoxide[11] than with aqueous sodium hydroxide[10] while the five haloforms that have been studied react 7–100 times as fast in aqueous solution as in methanol (probably partly because methoxide ion is a weaker base than hydroxide ion)[12] suggests that the dihalomethylene mechanism is more favored in water than in methanol.

**The Concerted Mechanism.**—Of the fifteen haloforms for which basic hydrolysis rates have been studied, the five most reactive all contain a fluorine atom to stabilize the intermediate dihalomethylene (and either a bromine or iodine atom to be lost as an anion in the rate-controlling step of the reaction).[4,5] The hydrolysis rate data thus seem to show that fluorine atoms stabilize dihalomethylenes (or at least the transition states leading to them) much better than other halogen atoms and, in fact, this hypothesis is supported by the results of quantitative correlation of the relative hydrolysis rates of haloforms.[5b] Since fluorine atoms (relative to other halogen atoms) retard carbanion formation while speeding dihalomethylene formation from haloforms, the replacement of other halogens by fluorine tremendously increases the tendency of trihalomethyl anions to decompose to dihalomethylenes.

From the fact that the hydrolyses of chloro- and bromodifluoromethane are so much faster than would even be expected for carbanion formation, we infer that the carbanion is not a real reaction intermediate in these cases. Apparently two fluorine atoms have added so greatly to the tendency of the carbanion to decompose to dihalomethylene that it decomposes as it forms. As the removal of the haloform hydrogen begins, the negative charge thus placed on carbon causes the synchronized cleavage of the carbon–chlorine (or bromine) bond.

$$HO^- + HCF_2Cl \longrightarrow \overset{-\delta \quad -\delta \quad -\delta}{HO\text{--}H\text{--}CF_2\text{--}Cl} \longrightarrow HOH + CF_2 + Cl^-$$

Each of the two processes helps the other. The greater the negative charge on carbon the more easily is the halide ion lost. The greater the extent to which the halide ion is lost, the more acidic is the hydrogen atom being removed by base. Thus it is possible to go directly to what is probably the most stable of the dihalomethylenes and by-pass what would be a relatively unstable trihalomethyl anion.

**The Hydrolysis of Deuterobromodifluoromethane.**—Our hypothesis that there is thus both a concerted and stepwise mechanism for α-eliminations is reminiscent of the similar duality of mechanisms for β-eliminations.[13] A method for testing for the carbanion mechanism for β-elimination as in other cases for which carbanion intermediates have been postulated is to see whether reaction of the starting material is accompanied by its deuterium exchange. We have applied this test to our reaction by studying deuterobromodifluoromethane. We prepared this compound by the action of mercuric fluoride on 94 ± 1% deuterobromoform and assumed that its deuterium content was the same. If its hydrolysis proceeds by a concerted mechanism to yield difluoromethylene and if the difluoromethylene is not reverted to haloform, then, unlike the other nine deuterohaloforms that have been studied,[5–7] deuterated bromodifluoromethane may *increase* in deuterium content as it hydrolyzes, since the protium compound would be expected to react faster due to a kinetic isotope effect.[14] The rate-controlling steps for the two isotopically different species will be

$$CDBrF_2 + OH^- \xrightarrow{k_1} HOD + CF_2 + Br^-$$

$$CHBrF_2 + OH^- \xrightarrow{k_2} HOH + CF_2 + Br^-$$

The two kinetic equations

$$\frac{dD}{dt} = k_1 D \text{ and } \frac{dH}{dt} = k_2 H$$

where $D = [CDBrF_2]$, and $H = [CHBrF_2]$, may be combined to give

$$\frac{dH}{dD} = \frac{k_2}{k_1}\frac{H}{D}$$

(10) E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A196**, 540 (1949).

(11) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

(12) J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).

(13) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, sec. 7-1a.

(14) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

ich, upon separation of variables, integration evaluation of the integration constant gives

$$\log \frac{H_0}{H} = \frac{k_2}{k_1} \log \frac{D_0}{D} \qquad (1)$$

e value of the kinetic isotope effect $k_2/k_1$ was de- mined directly (2.02 ± 0.14) by determining the e constant for the hydrolysis of the deuterohalo- n (Table I). The fact that this rate constant did climb significantly during the kinetic run wed that the hydrolysis reaction was not accom- ied by any large amount of deuterium exchange. addition we extracted the unreacted haloform n two reaction solutions and found that its deu- um content actually had increased, from 94% to 5 ± 1% after 31 ± 2% reaction and to 99.5 ± % after 92 ± 2% reaction. Since the values t may be calculated from eq. 1 are 95.5 and %, respectively, the amount of haloform that hanged hydrogen with the solvent was negligible.

**elation to Other α-Eliminations.**—Such α- inations with rearrangement as the formation iphenylacetylene from 2,2-diphenylvinyl halides base have been known for some time.[15] As iser has pointed out[16] these reactions may be certed or may proceed by as many as three s. In view of Bothner-By's evidence for some nerization of the intermediate anion[17] it seems able that this reaction involves at least two s. A somewhat similar α-elimination, the mann reaction of amides, is clearly stepwise.[16] o previously reported α-elimination does there ear to be any strong evidence for a concerted hanism. The dehydrohalogenation of *n*-octyl ride by potassium amide, a reaction that has reported to proceed partly by an α-elimina- mechanism, has been shown to be unaccompa- by deuterium exchange of the starting halide.[18] vever, this sort of evidence, like our observed exchange of deuterobromodifluoromethane, can explained reasonably by the assumption that e is a true intermediate carbanion but that it tically invariably loses a halide ion to complete α-elimination instead of coördinating with a on to revert to starting material. We feel that is much weaker evidence for a concerted mech- n than our observation that the loss of halide appears to add driving force to the proton re- al. The change of mechanism from stepwise to erted in such a related series as the haloforms ests that it may occur in other series too.

he reactivity of $CHF_2SF_5$ toward alkali in con- to the inertness of $CF_3SF_5$ suggests the occur- e of an α-elimination to give the difluoromeths e intermediate.[19] The fact that fluoroform is active suggests that the $SF_5$ group is more eas- lisplaced with its bonding electron pair than lorine.

hen it is considered that the halide ion being aced is certainly being solvated and that anion solvations is an acidic type of function,[20] our concerted mechanism is seen to be quite similar to the mechanism suggested by Horiuti, Tanabe and Tanaka[21] for the hydrolysis of chloroform, a reaction for which we have proposed a stepwise mechanism.

## Experimental

**Reagents.**—Bromodifluoromethane (du Pont) was used directly from the cylinder without further purification. Its infrared spectrum showed it to contain less than 1% dibromofluoromethane and less than 1% fluoroform. The chlorodifluoromethane used has been described previously.[2]

**Deuterobromodifluoromethane.**—Deuterobromodifluoromethane was prepared from bromoform by deuteration followed by reaction with mercuric fluoride. About 7.5 g. of anhydrous sodium carbonate was dissolved in 100 g. of 99.5+% deuterium oxide, and 20 ml. of this solution was shaken with 100 ml. of freshly distilled bromoform for 4 hr. The bromoform layer was then shaken with a fresh 20 ml. of $Na_2CO_3$–$D_2O$ solution for 17 hr. after which infrared measurements[8] showed it to be 84% deuterated. An additional 6 hr. of shaking with a third fresh portion of the heavy water and 16 hr. with a fourth batch yielded 95 ml. of 94 ± 1% deuterobromoform. The deuterobromoform was added gradually with stirring over a period of 1 hr. to 213 g. of mercuric fluoride, and then the reaction flask was heated until the unreacted bromoform distilled. While most of the product was deuterodibromofluoromethane, collected in the ice-cooled receiver, about 10 ml. of liquid was found in the Dry Ice trap. When the trap was allowed to warm the material distilling between pot temperatures of −15 and 18° was collected (about 3 ml.). This material was allowed to vaporize through a fritted glass tube into about 800 ml. of oxygen-free water at 0° until the distilling flask reached 0°. Extraction of a portion of the 800 ml. of aqueous solution with carbon disulfide and infrared measurements showed absorption maxima (in order of decreasing intensity) at 9.32, 8.76, 10.07, 9.00, 10.30, 11.29, 15.08, 10.48, 14.16, 10.64, 13.53 and 11.02 μ. Separate measurements on $CHBrF_2$, $CHBr_2F$ and $CDBr_2F$ showed the 9.00 and 14.16 μ maxima very probably to be due to $CHBrF_2$ and the 11.29 and 15.08 μ maxima due to $CDBr_2F$. We have assumed that the bromodifluoromethane prepared was 94 ± 1% deuterated just as the bromoform from which it was made. Infrared measurements showed that 1.5 ± 0.5 mole % of $CDBr_2F$ was also present. The addition of 0.15 ml. of 0.04877 *N* sodium hydroxide solution to 20 ml. of the aqueous $CDBrF_2$ solution containing phenolphthalein gave a strong pink color. This showed that there was present no more than 0.5% of materials that are acidic or that liberate acids very easily (compounds such as HF, $COBr_2$, $COF_2$, COBrF, etc.).

**Hydrolysis Kinetics.**—The kinetics of the alkaline hydrolysis were studied by techniques of which the following run with bromodifluoromethane at 0° is an example. About 500 ml. of an aqueous solution of bromodifluoromethane was prepared by bubbling the gas into a 500 ml. flask full of oxygen-free water and surrounded by a water-ice slurry. Eleven 40-ml. pipets full of this solution were removed in as rapid succession as possible. Further precautions to minimize loss of the haloform from the aqueous solution include the use of cold pipets and of nitrogen pressure to fill the pipets. The third and ninth samples were emptied into 100-ml. flasks containing 20 ml. of 0.1467 *N* carbonate-free sodium hydroxide solution and allowed to stand at 0° for 2 hr. They were then allowed to warm to room temperature (25°) during an hour and finally heated to 45° for 30 minutes to ensure complete hydrolysis of the haloform. Titration of the unreacted base with 0.06360 *N* perchloric acid showed that the haloform in sample 3 had been 0.02294 *N* and that in sample 9, 0.01917 *N*. The normality of a haloform solution toward base is equal to $3 + f$ times its molarity. Expression of our usual rate equation[3,4] in the form

$$k = \frac{2.303}{t(b - [3 + f]a)} \log \frac{(3 + f)a(b - [3 + f]x)}{b/([3 + f]a - [3 + f]x)}$$

P. Fritsch, *Ann.*, **279**, 319 (1894); see Bothner-By[17] for other ices.

C. R. Hauser, THIS JOURNAL, **62**, 933 (1940).

A. A. Bothner-By, *ibid.*, **77**, 3293 (1955).

D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor and C. R. Gra[illegible], *ibid.*, **74**, 5599 (1952).

G. A. Silvey and G. H. Cady, *ibid.*, **72**, 3624 (1950).

(20) Ref. 13, pp. 44, 47.

(21) J. Horiuti, K. Tanabe and K. Tanaka, *J. Research Inst. Catalysis*, Hokkaido Univ., III, No. 3, 119, 147 (1955). We do not comment any further on this work since we hope first to resolve our differences by collaborative experiments.

where $a = [CHX_3]_0$, $b = [OH^-]_0$, $x = \Delta[CHX_3]_t$, $t$ = time (in seconds), and $f$ = fraction of haloform that gives formate, shows that we need not know $f$ nor $a$ provided that we know the normality of haloform, $(3 + f)a$, and the change in hydroxide ion concentration, $(3 + f)x$. Each of the other nine 40-ml. samples of aqueous haloform solution was put in a 50-ml. volumetric flask at 0°. The haloform normalities of these solutions were calculated from the values found for the third and ninth samples with the assumption of a constant change in concentration between each two consecutive samples. The alternate assumption that the change is proportional to the concentration gives calculated normalities that never differ from those used by more than 0.8%. At recorded times, 10 ml. of 0.1470 $N$ sodium hydroxide solution at 0° was pipetted by a cold pipet into each of the nine 50-ml. volumetric flasks. The reactions were stopped at recorded times by pouring the contents of the volumetric flasks into 25 ml. of cold 0.06200 $N$ perchloric acid. Samples 1 and 2 were stopped within 30 seconds to serve as "zero points." The excess acid was titrated to the brom cresol purple end-point with 0.04877 $N$ carbonate-fr sodium hydroxide solution. The data obtained are giv in Table II.

TABLE II

HYDROLYSIS OF $CHBrF_2$ IN AQUEOUS SOLUTION AT 0°[a]

| Sample no. | Time[b] (sec.) | Δ Titer, ml. 0.04877 $N$ NaOH | $10^3k$ (l./mole sec.) |
|---|---|---|---|
| 4 | 690 | 0.69 | 1.924 |
| 5 | 1,235 | 1.21 | 2.005 |
| 6 | 2,125 | 1.88 | 1.918 |
| 7 | 3,060 | 2.48 | 1.885 |
| 8 | 6,110 | 4.50 | 1.985 |
| 10 | 8,080 | 5.58 | 2.167 |
| 11 | 11,035 | 6.55 | 2.095 |
| | | Av. | $1.997 \pm 0.079$ |

[a] $[NaOH]_0 = 0.02930$. [b] From the time the zero points (1 and 2) were taken.

Heats and entropies of activation were calculated from th absolute rate equation[22]

$$k = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

**Hydrolysis of Deuterobromodifluoromethane.**—The k netics of the hydrolysis of deuterobromodifluoromethane we studied by techniques like those described for the protiu compound in the previous section. The "uncorrected rate constant of $(1.09 \pm 0.03) \times 10^{-3}$ l./mole. sec. obtain was corrected to $(1.03 \pm 0.05) \times 10^{-3}$ by allowing for th presence of the more reactive protium compound and de terodibromofluoromethane. The isotopic analyses we carried out by extracting the aqueous reaction solution wi carbon disulfide and running the infrared spectrum of th extract. The per cent. protium compound present was ca culated by comparison of the 7.88 and 9.01 $\mu$ bands of CH $BrF_2$ with the 8.76 and 9.32 $\mu$ bands of $CDBrF_2$ in this e tract and also in an extract of the starting material and as suming that the starting material was 94% deuterate Any error in the assumption would result in a proportion error in the same direction in our analyses and would there fore have little effect on our conclusion that hydrolysis unaccompanied by deuterium exchange.

**Acknowledgments.**—We wish to acknowledge ou indebtedness to the "Kinetic" Chemical Division E. I. du Pont de Nemours and Company for sample of bromodifluoromethane.

(22) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y 1941, p. 14.

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# The Hydrolysis and Deuterium Exchange of Dibromofluoromethane and Fluorodiiodomethane

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[Contribution from the School of Chemistry of the Georgia Institute of Technology]

# The Hydrolysis and Deuterium Exchange of Dibromofluoromethane and Fluorodiiodomethane[1]

By Jack Hine, Richard Butterworth and Paul B. Langford

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Rate constants and heats and entropies of activation have been determined for the basic hydrolysis and the deuterium exchange of dibromofluoromethane and fluorodiiodomethane in aqueous solution. The hydrolysis of bromodichloromethane and dibromochloromethane also was studied. For all four haloforms the data support the hydrolysis mechanism in which dihalomethyl anions, formed reversibly from haloform and base, decompose to dihalomethylenes, reactive intermediates that react quickly, either with halide ions to regenerate haloform or with water and alkali to give carbon monoxide or formate ions. The effect of added salts on the rate of the hydrolysis of dibromofluoromethane is compared with their effect on bromochloromethane and dibromochloromethane in order to learn how variations in the structure of dihalomethylenes affect the efficiency with which the dihalomethylenes may be captured by halide ions. The intermediates, dichloromethylene and bromochloromethylene, are captured with roughly equal efficiency, while bromofluoromethylene is captured with much less efficiency, if at all. While the rate of exchange of deuterodibromofluoromethane was about that expected from data on other haloforms, deuterofluorodiiodomethane exchanged more rapidly than anticipated.

In earlier articles[2] evidence was presented to show that the basic hydrolysis of several haloforms involves the intermediate formation first of a trihalomethyl anion and then a dihalomethylene. In order to investigate the generality of this reaction mechanism for haloforms as well as to learn more about the effect of structure on reactivity in dihalomethyl anion and dihalomethylene formation, we have studied the hydrolysis and deuterium exchange of dibromofluoromethane and fluorodiiodomethane. We also have studied briefly the effect of the structure of dihalomethylenes on their ease of capture by halide ions.

## Results and Discussion

**Hydrolysis.**—Although the fluorodiiodomethane prepared by the reaction of iodoform with mercuric fluoride boiled higher than that reported by Ruff and co-workers[3] or by Haszeldine,[4] the agreement of the boiling point with that predicted from an empirical equation for correlating the boiling points of halomethanes[5] as well as the agreement of the molar refractivity and iodine analysis with the calculated values support the assignment of the $CHFI_2$ structure.

We have studied the hydrolysis of fluorodiiodomethane in aqueous solution at 0 and 20.85°. The rate constants were calculated from the equation used previously[2]

$$k = \frac{2.303}{t(a[3 + f] - b)} \log \frac{b(a - x)}{a(b - [3 + f]x)} \qquad (1)$$

where $a = [CHX_3]_0$, $b = [OH^-]_0$, $x = a - [CHCl_3]_t$, $t$ = time, $f$ = fraction of haloform that hydrolyzes to formate (the rest gives carbon monoxide), and $k$ is expressed in liters/mole of haloform × seconds. In Table I are listed these data and heats and entropies of activation calculated from the absolute rate equation[6]

$$k = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

Table I

Basic Hydrolysis of Dibromofluoromethane and Fluorodiiodomethane in Aqueous Solution

| | $CHBr_2F$ | $CHFI_2$ |
|---|---|---|
| $10^3k$ at 0° | 2.77 ± 0.03 | 0.153 ± 0.003 |
| $10^3k$ at 20.85° | 70.8 ± 2.9[a] | 6.15 ± .13 |
| $\Delta H^{\ddagger}$, kcal./mole | 25.7 ± 0.5 | 27.7 ± .3 |
| $\Delta S^{\ddagger}$, e.u. | 24.1 ± 2.0 | 25.6 ± 1.2 |

[a] At 19.6°.

Preliminary tests showed that dibromofluoromethane was the most reactive haloform that we have studied. The rate constants obtained in the first runs at 0° fell considerably as the reaction proceeded. This was found to be due to the temperature of the reaction solution being significantly above 0° for the first few minutes of the reaction.

(1) Part X in the series "Methylene Derivatives as Intermediates in Polar Reactions." For part IX, see ref. 21. This work was supported in part by the Office of Ordnance Research, U. S. Army.

(2) J. Hine, A. M. Dowell, Jr., and J. E. Singley, This Journal, **78**, 479 (1956), and references cited therein.

(3) O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltschitzky, *Z. anorg. Chem.*, **69B**, 299 (1936).

(4) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

(5) J. Hine and S. J Ehrenson, *J. Org. Chem.*, **21**, 819 (1956).

(6) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

Although the pipets used to introduce the base that initiated the reaction were chilled before use, they and their contents warmed several degrees during the process of transferring the solutions. The necessity of shaking the reaction flask and the exothermic nature of the reaction added to this effect. In previous runs with less reactive compounds, it had been possible to ignore the first few minutes of reaction and calculate $k$'s from data on the part of the reaction occurring after that time. In the present case, however, too much of the reaction took place during the first few minutes. We therefore calculated our rate constants by use of the following corrections.

The instantaneous rate constant at the higher temperatures occurring in our reaction ($k_t$) is related to the value at 0° ($k$) by the expression

$$k_t = k\, e^{E(T - 273)/273T}$$

where $T$ is the absolute temperature of the reaction solution at the time $t$ and $E$ is the Arrhenius activation energy. Substitution into the differential form of eq. 1 and rearrangement gives

$$\frac{dx}{(a - x)(b - [3 + f]x)} = k\, e^{E(T - 273)/273T}\, dt$$

Since the integral of the left side of this equation is simply $k_{unc}\, t$ where $k_{unc}$ is the uncorrected (falling) rate constant that we had calculated from eq. 1

$$k = \frac{k_{unc}}{t} \int_0^t e^{E(T - 273)/273T}\, dt \qquad (2)$$

a plot of $T$ *vs.* $t$ was made, and from this plot and a value of $E$ the integral in eq. 2 could be evaluated for any $t$. As a check on the validity of the method it was found that the value of $E$ that resulted in $k$'s having the least average deviation from the mean in five different runs was 27.7 ± 1.5 kcal./mole, in reasonable agreement with the value determined experimentally (26.2). The experimental value was the one used in calculating the $k$'s listed in Table I. The rate constants were determined at an ionic strength of about 0.10, but data on bromodichloromethane (Table II) and chloroform[7] show that haloform hydrolysis rates are not very sensitive to changes in ionic strength.

In addition to argument by analogy, there is much direct experimental evidence that diiodofluoromethane and dibromofluoromethane hydrolyze by the mechanism

$$CHX_3 + OH^- \rightleftharpoons CX_3^- + H_2O \qquad (I)$$
$$CX_3^- \longrightarrow CX_2 + X^-$$

followed by rapid reactions of the intermediate $CX_2$. Both compounds are reported herein to undergo base-catalyzed deuterium exchange more rapidly than they hydrolyze. Both are much more reactive than would be expected for the SN2 mechanism.[8] The reactivity of each of the compounds fits satisfactorily into a quantitative correlation of haloform reactivities based on the proposed mechanism.[12]

**Capture of Dihalomethylenes by Halide Ions.**—From the observed relative reactivities of haloforms it appears that, relative to chlorine, fluorine stabilizes dihalomethylenes and bromine destabilizes them.[2,12] We thought it of interest to determine how the presence of the various halogens affects the ease of capture of dihalomethylenes by such nucleophilic reagents as halide ions. It has been reported earlier that the addition of chloride ion slows the basic hydrolysis of chloroform, due to reversal of the second step of the reaction (see mechanism I).[7] Bromide and iodide bring about even larger "apparent" decreases in reaction rate (they decrease the rate at which alkali disappears), by combining similarly with dichloromethylene to yield haloforms. *e.g.*

$$CCl_2 + I^- \longrightarrow CCl_2I^- \xrightarrow{H_2O} CHCl_2I$$

We therefore studied the effect of various sodium salts at concentrations around 0.08 $M$ on the rate of the basic hydrolysis of dibromofluoromethane, dibromochloromethane and bromodichloromethane (as measured by the rate of disappearance of alkali). The rate constants obtained are shown in Table II.

TABLE II

EFFECT OF SALTS ON HALOFORM HYDROLYSIS IN AQUEOUS SOLUTION[a]

| Haloform | Salt | $10^5 k$, l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|
| $CHBr_2F$ | 0.080 $M$ NaF | 276 ± 8[b] |
| $CHBr_2F$ | .080 $M$ $NaClO_4$ | 277 ± 3[b] |
| $CHBr_2F$ | .080 $M$ NaBr | 276 ± 3[b] |
| $CHBr_2F$ | .080 $M$ NaI | 266 ± 2[b] |
| $CHBrCl_2$ | None | 1.49 ± 0.02[b] |
| $CHBrCl_2$ | 0.083 $M$ NaF | 1.47 ± .02[b] |
| $CHBrCl_2$ | .083 $M$ NaBr | 1.20 ± .02[b] |
| $CHBrCl_2$ | .083 $M$ NaI | 0.95[b,d] |
| $CHBrCl_2$ | .089 $M$ NaF | 1025 ± 20[c] |
| $CHBrCl_2$ | .089 $M$ NaBr | 783 ± 15[c] |
| $CHBrCl_2$ | .089 $M$ NaI | 590[c,d] |
| $CHBr_2Cl$ | .089 $M$ NaF | 562 ± 21[c] |
| $CHBr_2Cl$ | .089 $M$ $NaNO_3$ | 570 ± 30[c] |
| $CHBr_2Cl$ | .089 $M$ $NaClO_4$ | 551 ± 10[c] |
| $CHBr_2Cl$ | .089 $M$ NaBr | 428 ± 5[c] |
| $CHBr_2Cl$ | .089 $M$ NaI | 340[c,d] |

[a] $[OH^-]_0$ ~0.036 $M$ for $CHBr_2F$ and ~0.020 $M$ for other haloforms. [b] At 0°. [c] At 40°. [d] Falling rate constants extrapolated to zero time.

It was found earlier with chloroform that with such salts as sodium fluoride, nitrate and perchlorate, which would not be expected to be effective at capturing dihalomethylene intermediates, the reaction rate is essentially independent of the exact nature of the anion at concentrations below 0.16 $M$.[7] This observation, which was substantiated by measurements on dibromofluoromethane and dibromochloromethane, shows that the specific salt

(7) J. Hine and A. M. Dowell, Jr., THIS JOURNAL, **76**, 2688 (1954).

(8) The compounds are the α-fluoro derivatives of methylene bromide and methylene iodide, respectively. The α-fluoro substituent appears to decrease the SN2 reactivity in the cases that have been studied.[9,10] The reactivity of alkyl halides toward sodium hydroxide in water appears to be about the same as toward sodium methoxide in methanol.[11] Dibromofluoromethane is therefore about a million times as reactive as methylene bromide and diiodofluoromethane about fifty thousand times as reactive as methylene iodide.

(9) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955).

(10) J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

(11) Compare the data on methyl bromide and iodide in methanol from ref. 8 with that in water obtained by E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A196**, 540 (1949).

(12) J. Hine and S. J. Ehrenson, THIS JOURNAL, **80**, 824 (1958).

effects produced by bromides and iodides are very probably not due to such factors as ionic size, degree of solvation and ion-pair formation. Therefore the sharp decreases in the rate of hydrolysis of bromodichloromethane brought about by these two salts and their negligible effect on dibromofluoromethane show that dichloromethylene is much more effectively captured by bromide and iodide ions than is bromofluoromethylene. This interpretation is supported by the fact that the rate constants obtained in the presence of bromide ion showed no drift, since capture of dichloromethylene by bromide leads to re-formation of the starting haloform, while those obtained in the presence of iodide ion drifted downward during the reaction, since the less reactive haloform, dichloroiodomethane, was being formed. While the rate constants obtained with dibromofluoromethane and sodium iodide showed no appreciable drift, this may just mean that iodide ion did not capture bromofluoromethylene to any significant extent.

In order to learn whether the difference in behavior of dichloromethylene and bromofluoromethylene was due to the bromine or to the fluorine, we studied the intermediate, bromochloromethylene. This was done by measurements on dibromochloromethane, which, being somewhat less reactive, was studied at 40° rather than 0°. The results and analogous data on bromodichloromethane at 40° are listed in Table II and show that bromochloromethylene is captured approximately as effectively as dichlormethylene. This is shown more clearly in Table III where there are listed

TABLE III

COMPETITION FACTORS TOWARD THE DIHALOMETHYLENES FORMED FROM VARIOUS HALOFORMS

| Haloform | Ion | Temp., °C. | $k'/k$ | $k_x/k_w$ |
|---|---|---|---|---|
| $CHBr_2F$ | Bromide | 0 | ~1 | <50 |
| $CHBr_2F$ | Iodide | 0 | ~1 | <70 |
| $CHBrCl_2$ | Bromide | 0 | 0.816 | 159 |
| $CHBrCl_2$ | Bromide | 40 | .764 | 203 |
| $CHBrCl_2$ | Iodide | 0 | .646 | 386 |
| $CHBrCl_2$ | Iodide | 40 | .556 | 485 |
| $CHBr_2Cl$ | Bromide | 40 | .762[a] | 204 |
| $CHBr_2Cl$ | Iodide | 40 | .606[a] | 427 |

[a] Based on the average value, $k = 561 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$.

alues for the competition factors $k_x/k_w$

$$CY_2 + X^- \xrightarrow{k_x} CY_2X^-$$

$$CY_2 + H_2O \xrightarrow{k_w} \overset{\oplus}{H_2O}\text{–}\overset{\ominus}{CY_2}$$

alculated from the following equation, which was eveloped previously[7]

$$\frac{k_x}{k_w} = \frac{\left([H_2O] + \frac{k_h}{k_w}[OH^-]\right)\left(\frac{k}{k'} - 1\right)}{[X^-]}$$

here $k'$ is the rate constant in the presence of aX, $k$ that obtained with the same concentration an inert salt, and $k_h/k_w$ is the competition factor r hydroxide ion, *assumed* as before, to be equal to 29. The data on bromodichloromethane at the vo temperatures show that the values of $k_x/k_w$ e not *highly* temperature dependent. The values, particularly those of $k_{Br}/k_w$, having been determined from fairly small differences between two numbers each of which may be in error by several per cent., are not very precisely known, but the increase with temperature of $k_I/k_w$, at least, is probably meaningful. The values for bromodichloromethane are seen to be within the experimental error of those obtained previously for chloroform, as expected since both give the same intermediate, dichloromethylene.

It might have been expected that the fluorine-containing dihalomethylenes, being more stable, would have been able to discriminate better between the solvent water and the more nucleophilic halide ions.[13] We are not sure why they actually have less tendency to combine with halide ions. It is true that combination would lead to somewhat less stable trihalomethyl carbanions,[14] but if this were the sole explanation bromochloromethylene would show larger $k_x/k_w$ values than dichloromethylene. Any complete explanation should take into account the effect of structure on $k_w$ as well as $k_{Br}$. We know very little about the combination of water with dihalomethylenes, but if in some cases a proton donation to carbon is important the possibly more basic fluoromethylenes might be more reactive.

**Deuterium Exchange.**—The rates of carbanion formation of the haloforms were studied, as previously, by measuring the rate of the base-catalyzed hydrogen exchange of the deuteriohaloforms in "light" water solution. Preliminary measurements on diiodofluoromethane showed that the exchange reaction proceeded more than one hundred times as fast as the hydrolysis. Because of this and the fact that we used a buffer solution as the basic catalyst, the change in base concentration during a run was negligible. Therefore the following first-order rate equation derived previously was used in the calculation of rate constants.[15]

$$k[OH^-] + k'[CH_3NH_2] = \frac{2.303}{t}\log\left(\frac{D_0}{D_0 + H_0}\right)\left(1 + \frac{H}{D}\right) \quad (3)$$

$D = [CDFI_2]$, $H = [CHFI_2]$, $t$ = time (sec.). The ratio $H/D$ was determined by extraction of the reaction solution with isoöctane and infrared measurements. The hydroxide and methylamine concentrations at the ionic strength used were calculated from the data of Everett and Wynne-Jones.[16] Values of $k$ and $k'$ determined from runs at two different buffer concentrations but with the same buffer ratio are listed in Table IV as are heats and entropies of activation.[6]

In the case of dibromofluoromethane hydrolysis of the haloform is so extensive that the concentration of catalyzing base changes appreciably, even in the presence of a buffer, if the exchange re-

(13) Compare the increases in mass-law constants that accompany increasing stability of carbonium ions; L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940); C. G. Swain, C. B. Scott and K. H. Lohmann, THIS JOURNAL, **75**, 136 (1953).

(14) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

(15) J. Hine, R. C. Peek, Jr., and B. D. Oakes, *ibid.*, **76**, 827 (1954).

(16) D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc. (London)*, **A177**, 499 (1941).

TABLE IV

KINETIC DATA ON THE DEUTERIUM EXCHANGE OF DIIODOFLUOROMETHANE AND DIBROMOFLUOROMETHANE[a]

| Haloform | $CDFI_2$ | $CDBr_2F$ |
|---|---|---|
| $10^3k$ at 0° | 50.7 ± 1.4 | 20.7 ± 0.5 |
| $10^3k'$ at 0° | 0.027 ± 0.01 | 0.013 ± 0.005 |
| $10^3k$ at 20° | 823 ± 30 | 730 ± 20[b] |
| $10^3k'$ at 20° | 0.67 ± 0.3 | |
| $\Delta H^{\ddagger}$, kcal./mole[c] | 21.6 ± 0.5 | 22.5 ± 0.4 |
| $\Delta S^{\ddagger}$, e.u.[c] | 14.8 ± 2.0 | 16.1 ± 1.5 |

[a] All rate constants in l. mole$^{-1}$ sec.$^{-1}$. [b] At 25.05°. [c] For the hydroxide ion catalyzed reaction ($k$).

action is allowed to proceed to as much as half of completion. We have therefore followed the acidity of the reaction solution as well as the deuterium content of the haloform as the reaction proceeded. From acidimetric titrations we learned the change in the ionic strength and in the concentration of methylamine and for each point calculated the hydroxide ion concentration from data on the ionization of methylamine.[16] Plots of the hydroxide ion concentration *versus* the concentration of deuteriohaloform gave a smooth curve which could be fit well by an equation of the type

$$[OH^-] = [OH^-]_0 (1 - mz - nz^2) \qquad (4)$$

where $z$ is equal to $D_0 - D$ and $m$ and $n$ are constants whose optimum values are determined by the method of least squares. The simple rate equation

$$dz/dt = k(D_0 - z)[OH^-]$$

may therefore be combined with eq. 4 and integrated to give

$$k = \frac{2.303}{2(1 - mD_0 - nD_0^2)[OH^-]_0 t}\left[2 \log \frac{D_0}{D_0 - z} + \log (1 - mz - nz^2) - \frac{2nD_0 + m}{\sqrt{m^2 + 4n}} \log \frac{2 + z(\sqrt{m^2 + 4n} - m)}{2 - z(\sqrt{m^2 + 4n} + m)}\right] \qquad (5)$$

Rate constants calculated from this equation are in error, because we have neglected catalysis by methylamine. However, the observation that the values of $k$ obtained increase by less than 4% when the buffer concentration is more than doubled at constant buffer ratio and constant ionic strength shows that the methylamine catalysis and hence the error is not very large. By extrapolation of the rate constants from two such runs to zero buffer concentration the error may be removed and a value of $k'$, the catalysis constant for methylamine, determined. The data obtained are listed in Table IV.

While the reactivity of dibromofluoromethane fits satisfactorily into a quantitative correlation of the relative reactivities of haloforms (in carbanion formation),[17,18] it seems anomalous that fluorodiiodomethane should be more than twice as reactive in view of the fact that the replacement of the bromine atoms of bromoform or bromodichloromethane by iodine has virtually no effect on the carbanion formation rate. None of our explanations for this irregularity seem probable enough to warrant discussion here.

(17) See ref. 4, Fig. 2, where the rate constant used for deuteriodibromofluoromethane was a preliminary value, 13% smaller than the one now reported.

(18) Use of the present value would still give a satisfactory correlation.

## Experimental

**Reagents.**—The bromodichloromethane,[2] dibromochloromethane,[2] sodium salts,[7] sodium hydroxide solutions[7] and "oxygen-free" water[7] have been described previously. Dibromofluoromethane was prepared from bromoform and mercuric fluoride by the method of Thomas.[19] The properties of the material (b.p. 63° at 739 mm., m.p. below −78°, $d^{27.7}_4$ 2.2533, $n^{27.7}D$ 1.4628; molar refractivity calcd. 22.25, found 22.37) compared satisfactorily with those listed in the literature[20] (b.p. 64.9° at 757 mm., $d^{18.5}$ 2.4256). Deuteriodibromofluoromethane was prepared analogously from deuterated bromoform, the method having been described in detail in connection with the by-product deuterobromodifluoromethane.[21]

**Fluorodiiodomethane.**—Fluorodiiodomethane was prepared by a method based on that of Thomas.[19] Under a nitrogen atmosphere, 363 g. (0.92 mole) of iodoform was heated with stirring until it began to melt, when the heating was discontinued and 90 g. (0.377 mole) of anhydrous mercuric fluoride added slowly through an apparatus of the type described by Fieser.[22] After the addition was complete the temperature was held around 120° for about 15 minutes and the material was then distilled using a water aspirator vacuum. Between 60 and 105° (largely at 65–75°) 122 g. (56%) of purple liquid was obtained. This was washed with sodium thiosulfate solution, added to 50 g. of material from a run on 40% the scale, and fractionally distilled. The amber liquid boiling at 59.8–60.2° (50 mm.) weighed 97 g., m.p. −35 to −31° (mostly −32 to −31°), $d^{26.3}_4$ 3.1596, $n^{26.3}D$ 1.6496; molar refractivity calcd. 32.15, found 32.98. Ruff and co-workers[3] report m.p. −34.5° and $d^{14.4}_4$ 3.2206 and $d^{21.5}_4$ 3.1969, from which may be extrapolated $d^{26.3}_4$ 3.1809. They also report the vapor pressure at several temperatures between 26° (30.2 mm.) and 59.5° (113.3 mm.) and an equation relating the vapor pressure to temperature. They state that for this equation they calculate a b.p. of 100.3°, but our calculations using their equation show that a vapor pressure of 760 mm. would be expected at 122°. Haszeldine[4] reported a b.p. at 50 mm. of 50°, a temperature 12° higher than that for which Ruff's equation predicts a vapor pressure of 50 mm. An empirical equation from which may be calculated the boiling points of all of the measured halides of methane with an average deviation of less than three degrees predicts a boiling point of 142.6° for fluorodiiodomethane.[5,23] From a Trouton's rule constant of 21, b.p.'s of 133 and 145° (760 mm.) may be estimated from Haszeldine's and our data, respectively.

The infrared spectrum of the material is also reasonable for the assignment of the fluorodiiodomethane structure. In addition to the carbon–hydrogen stretching band at about 2950 cm.$^{-1}$ there is the rather strong absorption in the range 1000–1100 cm.$^{-1}$ said to be typical of monofluorides.[24] One of the bands in this latter range is, no doubt, analogous to the band (probably carbon–hydrogen deformation) that we have found between 1060 and 1220 cm.$^{-1}$ in all of the fourteen haloforms for which we have spectra. Furthermore, as for all the twelve haloforms we have observed, a new band appears in the range 740–820 cm.$^{-1}$ (at wave lengths differing by a factor of about $\sqrt{2}$ from 1060–1220 cm.$^{-1}$) for the deuterium compound.

*Anal.* Calcd. for $CHFI_2$: I, 88.80. Found (by reaction with excess alkali and titration by the Fajans method): I, 88.81, 88.85.

Deuteriofluorodiiodomethane was prepared similarly from deuterated iodoform[3] on a smaller scale. The product obtained after the final fractional distillation still had a

(19) C. H. Thomas, Ph.D. Thesis, Georgia Institute of Technology, 1953, p. 18.

(20) F. Swarts, *Bull. acad. roy. Belg.*, 113 (1910); *C. A.*, **5**, 1080 (1911).

(21) J. Hine and P. B. Langford, THIS JOURNAL, **79**, 5497 (1957).

(22) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., New York, N. Y., 1955, p. 265.

(23) The extrapolation of Haszeldine's b.p. to 122° cited in ref. 5 was done from a vapor pressure chart that has since been found to be considerably in error.

(24) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 270.

strong purple color, but titration with sodium thiosulfate showed that this was due to only 0.8% of iodine.

**Kinetics of Hydrolysis.**—The hydrolysis of dibromofluoromethane by aqueous sodium hydroxide at 0° was carried out in the following way. Into each of a number of 100-ml. volumetric flasks containing 80 ml. of 0.100 *M* salt solution was put 0.2500 ± 0.0008 ml. of dibromofluoromethane (at a known temperature) by use of a "tuberculin" syringe. The haloform was dissolved by vigorous shaking and the flask was returned to the 0° bath. When the material had reached thermal equilibrium 20 ml. of standard sodium hydroxide was introduced from a flask cooled in the same bath, by use of a pre-chilled pipet. To take a point the contents of a reaction flask (and two rinsings) were poured into a known volume (excess) of standard perchloric acid; the excess acid was then titrated to the phenolphthalein end-point with standard alkali. In several of the later points of several runs the concentration of bromide ion was determined by the Fajans method when the acidimetric titration was complete. From these data, values of $f$ for eq. 1 could be calculated. The average value obtained was 0.536. In the run at 19.6° the 80 ml. of haloform solution that went into every reaction flask was pipeted from a large flask in which the 0.250 ml. of dibromofluoromethane had been dissolved in one liter of 0.1 *M* sodium perchlorate. The solution at 0° was forced from this reaction flask into the 80-ml. pipets by nitrogen pressure, rather than being sucked, so as to avoid loss of the rather volatile haloform. An $f$-value of 0.536 was used at this temperature also since the data on fluorodiiodomethane as well as that on other haloforms[12,25] show that $f$ is only slightly dependent on the temperature (and $k$ is only slightly dependent on $f$).

The temperature of the reaction mixture in several runs at 0° that were not followed titrimetrically was measured by use of a thermocouple at intervals of a few seconds during the first part of the reaction and longer intervals later. The reaction run at 19.6° did not rise appreciably above this temperature, probably because the reactants were more dilute, the constant temperature bath was stirred and the room temperature was nearer the reaction temperature.

The hydrolysis of dibromochloromethane and bromodichloromethane at 40° was studied by a technique like that used for dibromofluoromethane at 19.6°, except that four to six times as much haloform was used. For these haloforms the first point was taken within a minute or two after the reaction was started. This was used as a "zero" point, corrections being applied to the data on the other points for the amount of reaction that occurred prior to the time of this point. In the runs on bromodichloromethane at 0°, the "one-flask-per-point" method was replaced by a technique in which the reaction flask contained several hundred milliliters of solution and points were taken by removing samples by pipet at various times. The value of $f$ used for bromodichloromethane was 0.15 (since the intermediate formed in this case is the same as with chloroform) and that found for dibromochloromethane was 0.164 (the difference between these two values is well within the experimental error).

The hydrolysis of fluorodiiodomethane at both temperatures used was studied by the method just described for bromodichloromethane at 0°. A value of $f$ of 0.362 was found at 0° and the value 0.34 at 20.85°. Carbon monoxide was shown to be a reaction product by infrared analysis of the gas above the reaction mixture at the end of one run.

**Kinetics of Deuterium Exchange.**—For the exchange of deuteriofluorodiiodomethane the following run is typical. To a solution of 0.16 ml. of deuteriohaloform in 400 ml. of oxygen-free distilled water containing 0.05 ml. of 0.08 *M* perchloric acid, to prevent exchange, was added 0.4 ml. of 0.1 *M* sodium thiosulfate to remove the iodine color. When this solution in a 500-ml. volumetric flask had equilibrated at 0°, 100 ml. of 0.4824 *M* methylammonium perchlorate–0.5606 *M* methylamine, also at 0°, was added. At measured times, 50-ml. samples were pipeted into excess acid and the D/H ratio determined by extraction with isoöctane and infrared measurement.

The exchange of deuteriodibromofluoromethane at 0° was carried out as follows. By use of a "tuberculin" syringe 1.00 ± 0.01 ml. (2.34 g.) of deuterated dibromofluoromethane was dissolved in 400 ml. of "oxygen-free" water in each of two 500-ml. volumetric flasks. After the flasks had reached thermal equilibrium in a 0° bath, 100 ml. of 0.0800 *M* methylamine–0.1005 *M* methylammonium perchlorate–0.150 *M* sodium perchlorate was added to flask no. 1 and 100 ml. of 0.2000 *M* methylamine–0.2513 *M* methylammonium perchlorate added to no. 2 (both buffers also at 0°). After about ten minutes (to be sure that the temperature was 0° again), a "zero point" was taken by withdrawing a 75-ml. sample from no. 1 and a 25-ml. sample from no. 2, each into a known volume (excess) of standard perchloric acid. The excess acid was titrated to the brom cresol purple end-point with standard sodium hydroxide and then 4 ml. of 1.2 *M* perchloric acid was added to ensure the transformation of all methylamine to its conjugate acid. The solutions were then extracted with isoöctane and infrared measurements carried out to determine the isotopic content of the haloform. Subsequent points were taken similarly and some later points were titrated for the bromide ion content by the method of Fajans, in order to permit the calculation of $f$. In calculating the hydroxide ion concentration at various points it was assumed that all of the methylamine used up was transformed to methylammonium ion, that is, that the reaction followed only the equations

$$CHBr_2F + 4CH_3NH_2 + 2H_2O \longrightarrow 4CH_3NH_3^+ + 2Br^- + F^- + HCO_2^-$$

and

$$CHBr_2F + 3CH_3NH_2 + H_2O \longrightarrow 3CH_3NH_3^+ + 2Br^- + F^- + CO$$

It is plausible that N-methylformamide and methyl isocyanide also may have been formed, but our observation that 3.44 moles of base reacted per mole of haloform showed that no more than 13% (100 × 0.44/3.44) of the methylamine that reacted could have given these products. Details of the data from run 2 are given in Table V. The calculated rate constants seem to climb slightly as the reaction proceeds. The possible error concerning the assumption involving $f$ mentioned above could have caused as much as a 1% climb. The neglect of general base catalysis in the derivation of eq. 5 could not only cause the average value of $k$ to be too high (this is corrected for, in extrapolating to zero buffer concentration) but could also cause a climb of about 0.2% in $k$.

TABLE V

KINETICS OF THE HYDROGEN EXCHANGE OF DEUTERIODIBROMOFLUOROMETHANE IN AN AQUEOUS METHYLAMINE BUFFER

$[CH_3NH_2]_0 = 0.03993$, $[CH_3NH_3ClO_4]_0 = 0.05022$, $[CDBr_2F]_0 = 0.02143$, $[CHBr_2F]_0 = 0.00295$, $m = 13.74$, $n = 839.47$

| Time, sec. | Aml., 0.0487 *N* NaOH | Optical density 11.226 $\mu$ | Optical density 14.204 $\mu$ | $\frac{D}{H+D}$ | [CD-$Br_2F$] | 100$k$, l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|---|---|
| 58,140 | 2.29 | 0.218 | 0.315 | 0.5602 | 0.01293 | 2.143 |
| 69,060 | 2.90 | .264 | .449 | .5195 | .01181 | 2.169 |
| 77,880 | 3.15 | .212 | .411 | .4869 | .01100 | 2.187 |
| 88,080 | 3.50 | .237 | .513 | .4594 | .01029 | 2.160 |
| 106,680 | 4.19[a] | .253 | .195[b] | .4489 | .00988 | 1.899[a] |
| 150,420 | 5.69 | .171 | .226[b] | .3169 | .00669 | 2.220 |
| 154,020 | 5.75 | .191 | .203[c] | .3020 | .00638 | 2.280 |
| | | | | | Av. | 2.193 ± 0.032 |

[a] The titration on this point was clearly out of line with those on the other points, and the infrared analysis led to a $k$ deviating from the mean by about six times the average deviation. The data on the point was therefore neglected. [b] The isoöctane solution for this determination was diluted to one-third the strength of that measured at 11.226 $\mu$. [c] One-fourth as strong as at 11.226 $\mu$.

Since practically all of the reaction was due to hydroxide ion and only a minor part to methylamine, at 25.05° data was taken at only one initial buffer concentration. A value of 0.350 was determined for $f$ under these conditions. From the values for dibromofluoromethane at 0° and fluorodiiodomethane and other haloforms at several temperatures[14,15] the value $7.4 \times 10^{-4}$ was estimated for $k'$ at 25°. By use of this value the average value of $k$ $(78.7 \pm 1) \times 10^{-2}$ ob-

(25) Unpublished observations from this Laboratory.

tained from eq. 5 was corrected to give the value shown in Table IV.

The apparatus and methods of infrared analysis and of calculation of the extent of deuteration of deuterated haloforms have been described previously.[12] The following extinction coefficients were used in the present work. For $CHFI_2$, $\epsilon_{9.173}$ 428.4 ± 0.6, $\epsilon_{9.475}$ 171 ± 0.4, $\epsilon_{9.622}$ 70.4 ± 0.8, $\epsilon_{9.752}$ 272.9 ± 1.6, $\epsilon_{12.154}$ 0.00 ± 0.2; $CDFI_2$, $\epsilon_{9.173}$ 200.2 ± 0.4, $\epsilon_{9.475}$ 110.8 ± 2.5, $\epsilon_{9.622}$ 260 ± 3.1, $\epsilon_{9.752}$ 157 ± 1.2, $\epsilon_{12.154}$ 308.4 ± 3.1; $CHBr_2F$, $\epsilon_{11.226}$ 324.5 ± 2.5, $\epsilon_{14.204}$ 0.00 ± 0.2; $CDBr_2F$, $\epsilon_{11.226}$ 0.00 ± 0.2, $\epsilon_{14.204}$ = 597 ± 8.

**Acknowledgment.**—The authors wish to thank Dr. Stanton J. Ehrenson for checking many of the calculations and derivations carried out during this investigation.

ATLANTA, GEORGIA

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Technical Report No. 4

# THE EFFECT OF STRUCTURE ON THE RELATIVE STABILITY OF DIHALOMETHYLENES

Contract No. DA-01-009-ORD-431

by

Jack Hine and Stanton J. Ehrenson

[Reprinted from the Journal of the American Chemical Society, **80**, 824 (1958).]

# The Effect of Structure on the Relative Stability of Dihalomethylenes

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[Contribution from the School of Chemistry of the Georgia Institute of Technology]

# The Effect of Structure on the Relative Stability of Dihalomethylenes[1]

By Jack Hine and Stanton J. Ehrenson

Received August 26, 1957

The relative reactivities of ten haloforms toward hydrolysis in aqueous solution are correlated in terms of an equation based on the dihalomethylene reaction mechanism. This equation uses the known carbanion formation rate constants and contains parameters for (1) the relative abilities of the various halogens to stabilize dihalomethylenes, (2) the relative ease with which halogens are separated as anions from the intermediate trihalomethyl anion, and (3) the carbanion character of the transition state for dihalomethylene formation. From the values of these parameters, halogens appear to facilitate dihalomethylene formation in the order $F \gg Cl > Br > I$. Since the dihalomethylenes appear to be non-radicals rather than diradicals, this order is attributed to the relative abilities of the halogens to supply electrons to the carbon atom by tautomeric effects. The relative electrophilic and nucleophilic characters of several methylenes are discussed in terms of these parameters. The parameters for the differences between the abilities of halogens to separate as anions ($Br > I > Cl$) are smaller and probably less significant. The transition state for dihalomethylene formation appears to have considerable carbanion character. For the basic decomposition reactions in methanol and aqueous dioxane, where carbanion formation rates are not known, equations are developed for correlating the data on smaller groups of haloforms. When an inhibitor is used to prevent the free radical reactions that occur with certain haloforms in these solvents, the rate constants obtained fit the equations satisfactorily.

## Introduction

In earlier articles of this series evidence was presented that at least some haloforms undergo alkaline hydrolysis by the mechanism

$$CHX_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CX_3^- + H_2O \qquad (I)$$

$$CX_3^- \xrightarrow{k_2} CX_2 + X^-$$

followed by rapid reactions of $CX_2$. Some of the first evidence that haloforms hydrolyze by this mechanism was the fact that their reactivities are so much greater than would be expected from the SN2 mechanism.[2] Since mechanism I explains the great reactivity of haloforms in general, toward basic hydrolysis, we hoped to be able to use this mechanism in correlating the relative reactivities of different haloforms, thus learning more about the ease of formation and hence perhaps the relative stabilities of various dihalomethylenes. We obtained data on the relative reactivities of six haloforms in 66⅔% dioxane–water solution,[3] which would have sufficed for a *qualitative* discussion of the effect of structure on reactivity, but by this time it was beginning to appear that the relative reactivities might be correlated *quantitatively* if values of $k_1$, the rate constant for the initial carbanion formation, were available. Unfortunately, these values were not available and, in fact, would be rather difficult to determine in such a solvent.[4] However, the kinetics of carbanion formation from haloforms may be studied by deuterium exchange experiments in purely aqueous solution, and data on a number of haloforms have been obtained in this solvent.[5-8] We therefore have determined rate constants for the basic hydrolysis of a number of haloforms in aqueous solution and correlated these rate constants in terms of the values of $k_1$ and of certain additional parameters by use of an equation based on mechanism I.

## Discussion and Results

**The Correlation Equation.**—In terms of the rate constants for the individual steps of the reaction, the over-all rate constant for hydrolysis may be expressed

$$k_h = \frac{k_1(k_2/k_{-1})}{1 + (k_2/k_{-1})}$$

Since the values of $k_1$ are known (or may be closely approximated by estimating the kinetic isotope effect), a correlation of the values of $k_2/k_{-1}$ is equivalent to a correlation of $k_h$ values. The fraction $k_2/k_{-1}$ is simply the rate constant by which the trihalomethyl anion yields dihalomethylene divided by the rate constant for its abstraction of a proton from water to re-form haloform.

The generality of applicability of the Brönsted catalysis law shows that the acids that donate pro-

(1) Part XI in the series "Methylene Derivatives as Intermediates in Polar Reactions." For part X see preceding paper. This work was supported in part by the Office of Ordnance Research, U. S. Army, and was presented in preliminary form at the Sixth Biannual Conference on Reaction Mechanisms, Swarthmore, Pa., Sept. 13, 1956.

(2) J. Hine, This Journal, **72**, 2438 (1950).

(3) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956).

(4) The dioxane would be extracted, with the haloform, in the first step of the isotopic analysis in the required deuterium exchange experiments.

(5) J. Hine, R. C. Peek, Jr., and B. D. Oakes, This Journal, **76**, 827 (1954).

(6) J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

(7) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

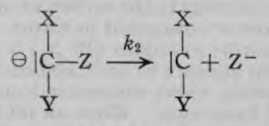
(8) J. Hine, R. Butterworth and P. B. Langford, *ibid.*, **80**, 819 (1958).

tons most rapidly are usually those whose conjugate bases accept protons the slowest. While the number of exceptions to this generalization is considerable,[9] we shall assume that it holds for the haloforms, particularly since they form a series of closely related compounds and their acid–base reactions should not be complicated by such things as internal rotation and steric inhibition of resonance. Putting this generalization in a quantitative form and using chloroform as a reference compound

$$\log \frac{k_{-1}^{CHXYZ}}{k_{-1}^{CHCl_3}} = -c \log \frac{k_1^{CHXYZ}}{k_1^{CHCl_3}} \qquad (1)$$

where $c$ is a dimensionless proportionality constant that may be thought of as the amount of change in carbanion character between the trihalomethyl anion and the transition state for its protonation divided by the change in carbanion character between the haloform and the transition state for carbanion formation.

We assume that three factors control the relative values of $k_2$.



One factor relates to the ease with which the halogen (Z in the equation above) that is departing as an anion in the transition state breaks away from carbon with its bonding electron pair. The second factor relates to the ability of the two halogen atoms (X and Y above) that remain attached to carbon to stabilize the dihalomethylene that is being formed in the transition state. The existence of the third factor depends on the fact that the carbanion character of the reactant is decreasing in the transition state. Therefore whatever tends to stabilize a carbanion will lower $k_2$. Assuming that the factors that control carbanion stabilization are adequately measured by $k_1$ and that the effects of changes in various factors on the free energy of activation will be linear, we arrive at the following equation in which the reactivity is expressed relative to chloroform as a standard.

$$\log \frac{k_2^{CHXYZ}}{k_2^{CHCl_3}} = M_X + M_Y + N_Z + \log \frac{n_Z}{3} - d \log \frac{k_1^{CHXYZ}}{k_1^{CHCl_3}} \qquad (2)$$

$M_X$ and $M_Y$ are the methylene stabilization factors for the two halogens that become a part of the dihalomethylene; $N_Z$ is a constant for that halogen being lost as an anion in the transition state; log $(n_Z/3)$ is a statistical factor in which $n_Z$ is the number of halogens of the type being lost and the "3" refers to the fact that there are 3 of these in chloroform; and $d$ is a dimensionless proportionality constant (assumed, like $c$, to be the same for all haloforms) for the trihalomethyl anion, being equal to the amount of carbanion character it has lost in the transition state for protonation divided by that lost in the transition state for dihalomethylene formation. Our use of chloroform as the reference compound defines $M_{Cl}$ and $N_{Cl}$ as zero.

(9) *Cf.* R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953).

Combining equations 1 and 2 we obtain

$$\log \frac{(k_2/k_{-1})^{CHXYZ}}{(k_2/k_{-1})^{CHCl_3}} = M_X + M_Y + N_Z + \log \frac{n_Z}{3} + (c - d) \log \frac{k_1^{CHXYZ}}{k_1^{CHCl_3}} \qquad (3)$$

This equation, of course, predicts only that part of the haloform hydrolysis rate that is due to the loss of halogen anions of the type of Z. While it should be used in the form shown for symmetrical haloforms (in which X = Y = Z), with "mixed" haloforms the total reaction rate is equal to the sum of the rates for reaction *via* loss of halogens of each of the kinds present.

**Correlation in Aqueous Solution.**—In order to test equation 3, rate constants were determined for the hydrolysis of a number of haloforms in aqueous solution at several temperatures. Determinations were made for all of the compounds for which deuterium exchange data are available except for iodoform, whose low solubility, low reactivity and great sensitivity to air and light made such measurements inconvenient. The resultant data are listed in Table I. All of the haloforms studied appear to hydrolyze by the dihalomethylene mechanism. Rate retardation by added halide ions ("mass-law effect") has been observed for chloroform,[2] bromodichloromethane[8] and dibromochloromethane.[8] The reaction of these three haloforms and of bromoform with sodium *p*-thiocresolate has been found to be catalyzed by base.[3] All of the compounds are known to undergo base-catalyzed deuterium exchange and to hydrolyze much more rapidly than would be expected, by extrapolation from data on methyl[10,11] and methylene halides,[3,11] by the SN2 mechanism.[12]

For seven of the haloforms, we had available only the rate constants for carbanion formation from the deuteriohaloforms. From these we calculated $k_1$'s, the values for the protium compounds, by use of deuterium kinetic isotope effects of 1.75 at 0° and 1.43 at 50°, these values being the average of those found at 0° and extrapolated to 50° for dichlorofluoromethane[6] and bromochlorofluoromethane,[7] the two haloforms for which kinetic isotope effects have been determined. The $k_1$ values for chlorodiiodomethane were assumed to be the same as those for chlorodibromomethane since the values for bromoform and iodoform are essentially equal as are those for dichloroiodomethane and bromodichloromethane at 0°. Because of this latter near-equality at 0°, $k_1$ for bromodichloromethane at 50° was assumed to be equal to $k_1$ for dichloroiodomethane at 50°. Rate constants were extrapolated to 0 and 50° when necessary by use of plots of log $k$ *vs.* $1/T$.

Optimum values of the parameters of eq. 3, calculated by the method of least squares, are listed in Table II. The values of log $(k_2/k_{-1})$ at 0° calculated from these parameters are listed in Table

(10) E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A196**, 540 (1949).

(11) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

(12) For the significance of the terms SN2 and SN1 see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., Chap. 5.

TABLE I

KINETIC CONSTANTS FOR THE BASIC HYDROLYSIS OF HALOFORMS IN AQUEOUS SOLUTION

| Compound | $10^4 k_1$, l. mole$^{-1}$ sec.$^{-1}$ 0.0° | 20.0° | 35.0° | 50.0° | $\Delta H^\ddagger$, kcal./mole | $\Delta S^\ddagger$, e.u. |
|---|---|---|---|---|---|---|
| $CHCII_2$ | 0.0010[a] | | 112 ± 25[b,c] | 9.2 ± 0.3 | 31.3 ± 3.0 | 24.2 ± 10 |
| $CHCl_3$ | .0060 ± 0.0004 | 0.23 ± 0.01 | 2.41 ± 0.03 | 18.8 ± 0.6 | 27.7 ± 0.5 | 14.4 ± 2 |
| $CHBr_3$ | .0240[a] | 1.99 ± .03[d] | 9.54 ± .14 | 84 ± 3[e] | 28.1 ± .3 | 18.6 ± 1 |
| $CHCl_2I$ | .0260[a] | 2.17 ± .03[d] | 11.6 ± .8[e] | 95 ± 6[e] | 28.3 ± .5 | 19.7 ± 2 |
| $CHBr_2Cl$ | .0665 ± 0.002[e] | | 56 ± 2[e,f] | 220 ± 13[e] | 27.9 ± .5 | 19.9 ± 2 |
| $CHCl_2F$[g] | .123 ± .001 | 3.95 ± 0.04[h] | | 300[m] | 26.8 ± .3 | 17.2 ± 1 |
| $CHBrCl_2$ | .149 ± .002[e] | 102 ± 2[e,f] | 49 ± 3 | 354 ± 8 | 27.1 ± .5 | 18.9 ± 2 |
| $CHFI_2$[e] | 1.53 ± .03 | 61.5 ± 1.3[i] | | 4900[m] | 27.8 ± .5 | 25.9 ± 3 |
| $CHBrClF$[j] | 13.2 ± .2 | 150 ± 5[k] | | 18000[m] | 24.8 ± .5 | 19.2 ± 2 |
| $CHBr_2F$[e] | 27.7 ± .3 | 708 ± 30[l] | | 50000[m] | 25.7 ± .5 | 24.1 ± 2 |

[a] Extrapolated from data at higher temperatures. [b] At 67.1°. [c] Rate constant determined graphically. [d] At 25.0°. [e] Data from ref. 8. [f] At 40°. [g] Data from ref. 6. [h] At 20.2°. [i] At 20.85°. [j] Data from ref. 7. [k] At 15.0°. [l] At 19.6°. [m] Extrapolated from data at lower temperatures.

TABLE II

VALUES OF THE PARAMETERS OF EQUATION 3

| | 0° | 50° | | 0° | 50° |
|---|---|---|---|---|---|
| $M_F$ | 3.727 | 3.193 | $N_{Br}$ | 0.785 | 0.936 |
| $M_{Br}$ | −1.461 | −1.131 | $N_I$ | .118 | .486 |
| $M_I$ | −2.626 | −2.039 | $(c - d)$ | .299 | .196 |

III with the values calculated from the experimental data. The average deviation, 0.027, corresponds to a 6% average error in the haloform hydrolysis rate constants that may be calculated from eq. 3. This is no larger than the probable error in the experimental determination of $k_2/k_{-1}$. At 50°, where more of the rate constants (including all of those for carbanion formation) were calculated by extrapolation, the average deviation was 0.053 or 13% in the rate constants.

TABLE III

COMPARISON OF EXPERIMENTAL VALUES OF LOG $(k_2/k_{-1})$ WITH THOSE CALCULATED FROM EQUATION 3 AT 0°

| Haloform | $-\log (k_2/k_{-1})$[a] Exptl. | Eq. 3 | Haloform | $-\log (k_2/k_{-1})$[a] Exptl. | Eq. 3 |
|---|---|---|---|---|---|
| $CHCII_2$ | 6.400 | 6.377 | $CHBrCl_2$ | 3.532 | 3.593 |
| $CHBr_3$ | 5.626 | 5.649 | $CHFI_2$ | 2.763 | 2.785 |
| $CHCl_2I$ | 4.267 | 4.267 | $CHBrClF$ | 0.246 | 0.208 |
| $CHBr_2Cl$ | 4.577 | 4.545 | $CHBr_2F$ | 1.082 | 1.069 |
| $CHCl_2F$ | 1.071 | 1.100 | | | |

[a] Based on the value 4.137 for chloroform.

The use of as many as six parameters to correlate nine values of log $(k_2/k_{-1})$ may seem to detract from the argument that the observed agreement with eq. 3 supports the proposed reaction mechanism. It is our feeling, however, that the evidence for the reaction mechanism is already adequate, and that since the three factors corresponding to the $M$, $N$ and $c$-$d$ parameters are certainly those that should logically be related to reactivity by this mechanism, these factors are best measured by some quantitative correlation such as eq. 3.

The correlation was made on the assumption that in a haloform containing both chlorine and bromine or chlorine and iodine, the reaction involves almost entirely the loss of bromide or iodide ion in the rate-controlling step, with chloride ion loss being only a negligible side reaction. The values of the parameters obtained justify this assumption. From eq. 3 it follows that if $k_2^{Cl}$ is the rate constant for the rate-controlling loss of chloride ion from the mixed haloform, $CHX_nCl_{3-n}$, and $k_2^X$ is the rate constant for the loss of the other halide, then

$$\log \frac{k_2^X}{k_2^{Cl}} = N_X - M_X + \log \frac{n}{3 - n} \qquad (4)$$

Calculations using eq. 4 show that in none of the bromine- or iodine-containing haloforms studied should the rate-controlling loss of chloride ion comprise more than 2% of the total reaction. It also seems very unlikely that the loss of fluoride ion is a significant part of any reaction. Our consideration of only one reaction path for each of our haloforms is therefore justified. With haloforms containing both bromine and iodine, however, the loss of each may contribute significantly to the reaction as a whole.

**Interpretation of the Parameter Values.**—The largest of the parameters of eq. 3 are the $M$-values. The $M_F$ and $M_I$ values (at 0°) show that the replacement of one iodine atom of a trihalomethyl anion by a fluorine lowers the activation energy for dihalomethylene formation by 8 kcal./mole, corresponding to an effect on $k_2/k_{-1}$ of more than two-million fold. Our interpretation of these $M$-values, however, must depend on whether the dihalomethylenes being formed are in the singlet (non-radical) or triplet (diradical) state. From the magnitudes of the bathochromic shifts in the ultraviolet spectra of alkyl iodides that are produced by various substituents, it appears that $\alpha$-halogens have the following relative abilities to stabilize free radicals: I > Br > Cl > F.[13] This conclusion is supported by determinations of the bond dissociation energies of various aliphatic iodides[14] and bromides[15] and to some extent by data on the relative reactivities of halomethanes toward sodium in the vapor phase.[16] Thus if triplet dihalomethylenes were being formed we might have expected the order $M_I > M_{Br} > M_{Cl} > M_F$. On the other hand if a singlet is being formed the process is simply an SN1 reaction[12] of a carbanion, and

(13) R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953).

(14) E. T. Butler, E. Mandel and M. Polanyi, *Trans. Faraday Soc.*, **41**, 298 (1945); F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 1489 (1954).

(15) M. Szwarc and A. H. Schon, *ibid.*, **19**, 656 (1951).

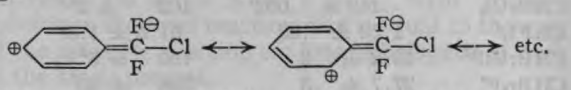
(16) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, chap. XIII.

α-halogen substituents might be expected to have the same effect that they do in other SN1 reactions. However, in the only case that appears to have been studied, α-halogens facilitated SN1 reactivity in the order Cl > Br > F.[17]

Since neither the radical nor non-radical mechanism permits a satisfactory *prediction* of our *M*-values from reactivity data in reactions of known mechanism, we must distinguish between these possibilities on the basis of other evidence. The singlet structure for dihalomethylenes, in which the carbon atom is left with a vacant orbital, is in agreement with the considerable evidence that these species behave as electrophilic reagents. Thus, for example, there is a linear relationship between the nucleophilicities of halide ions and their relative reactivities toward dichloromethylene that extends even to the amphoteric reagent water.[18] Analogously Skell and Garner have found that the reactivities of olefins toward dibromomethylene are increased by electron-donating substituents.[19] The facts that the relative reactivities of olefins toward dibromomethylene do *not* parallel their reactivities toward halomethyl radicals[19] and that the additions of dibromomethylene and even methylene itself to olefins are stereospecifically *cis*[20] provide even more evidence for the non-radical nature of dihalomethylenes.

Another strong argument that dihalomethylenes have a singlet (and non-linear) structure is based on theoretical and spectroscopic considerations. Walsh has reviewed and re-emphasized the evidence that the geometry of molecules of the B–A–C type is determined by the number of valency electrons.[21] Each of the seven species having eighteen valency electrons upon which he quotes structural data has a bond angle in the range 120 ± 10° and each is a singlet. These include the species NOCl and NOBr, which are isoelectronic with our intermediates, CFCl and CFBr. Even more directly relevant are the data on $CF_2$, a dihalomethylene, although not an intermediate in any of the hydrolyses studied herein. The spectrum of this molecule offers evidence for a non-linear singlet structure.[21,22] With the dihalomethylenes derived from the higher halogens, the triplet state should be lower-lying with respect to the singlet than is the case with $CF_2$, and it is possible the triplet is the more stable form in $CI_2$. Nevertheless we shall assume that the trihalomethyl anions lose halide ions to give dihalomethylenes without concomitant change in multiplicity.

On this basis we attribute the observed order, $M_F >> M_{Cl} > M_{Br} > M_I$, to the relative abilities of the four halogens to supply electrons to the deficient carbon atom. This sequence agrees with Taft's recent quantitative evaluation of the relative ability of the halogens to supply electrons by resonance[23] as well as with earlier qualitative assessments of the positive electromeric and mesomeric effects.[24] The observed greater reactivity of $C_6H_5CCl_3$ compared to $C_6H_5CF_2Cl$, upon which was based the conclusion that α-chlorine facilitates SN1 reactivity better than α-fluorine,[17] may be due to several factors that do not influence the SN1 reactivity of trihalomethyl anions. For example, the benzodifluorochloride must be stabilized by the contribution of such resonance structures as[25]




This resonance, which has no analog in the trihalomethyl anion, would be lost during carbonium ion formation.

Since the relative ability to stabilize carbanions appears, from the deuterium exchange data, to stand in the order Br > Cl > F, while the ability to stabilize the electron deficiency of methylenic carbon atoms appears, from the *M*-values, to vary in the order F > Cl > Br, it might be expected that the relative electrophilic character of dihalomethylenes would vary in the order $CBr_2 > CCl_2 > CF_2$, with the relative order of nucleophilicity varying in the opposite order. Recent studies on the mechanism of the basic hydrolysis of chlorodifluoromethane and bromodifluoromethane give more direct evidence for this point of view. From their reactivities as well as a deuterium-exchange study it appears that the basic hydrolysis of these two haloforms, is a concerted process in which the bromide or chloride ion is lost *as* the hydrogen atom is removed, difluoromethylene being formed in a single step not involving a carbanion intermediate.[26] From the principle of microscopic reversibility it follows that difluoromethylene, in combining with a chloride or bromide ion,[27] simultaneously accepts a proton from water. That is, in its reaction with chloride and bromide ions in aqueous solution difluoromethylene simultaneously displays both electrophilic and nucleophilic character, in contrast to dichloromethylene which acts purely as an electrophilic reagent, combining with nucleophilic halide ions to give trihalomethyl anions that are protonated only subsequently. With the recently reported alkoxyfluoromethylene intermediates[28] even more nucleophilic and less electrophilic character would be expected. In fact, it would not be surprising if these intermediates reacted with hydroxylic solvents by proton abstraction to give $ROCHF^+$ type carbonium ions.

The *N* parameters, relating to the ease of separation of the halogens as anions, correspond to bromine reacting 6–8 and iodine 1.3–3 times as fast as chlorine. While the reactivity series Br > I > Cl is not the one most commonly observed

(17) J. Hine and D. E. Lee, THIS JOURNAL, **73**, 22 (1951); **74**, 3182 (1952).

(18) J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

(19) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(20) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956); P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

(21) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

(22) P. Venkateswarlu, *Phys. Rev.*, **77**, 676 (1950); R. K. Laird, E. B. Andrews and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950).

(23) R. W. Taft, Jr., THIS JOURNAL, **79**, 1045 (1957).

(24) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 75, 89.

(25) *Cf.* J. D. Roberts, R. L. Webb and E. A. McElhill, THIS JOURNAL, **72**, 408 (1950).

(26) J. Hine and P. B Langford, *ibid.*, **79**, 5497 (1957).

(27) D. C. Duffey has obtained evidence for the occurrence of these reactions in this Laboratory.

(28) J. Hine and K. Tanabe, THIS JOURNAL, **79**, 2654 (1957); J. Hine and J. J. Porter, *ibid.*, **79**, 5493 (1957).

in nucleophilic displacement reactions of saturated aliphatic halides, it has been reported on more than one occasion.[10,11] Even after allowing for errors in determination (parameter values differing from those listed by about 0.2 can be obtained without more than doubling the average deviation of calculated from experimental $k_2/k_{-1}$ values) our $N$-values seem rather small, since an incomplete literature survey[11,17,29] that located more than sixty ratios of the reactivity of bromides or iodides to that of chlorides revealed $k^{RBr}/k^{RCl}$ values ranging from 11[29a] to 1520[29b] and $k^{RI}/k^{RCl}$ values ranging from 4[29a,c] to 735.[29d] It may be that for some reason, perhaps related to the carbanionic character of the reactant, the relative reactivities of bromides and iodides are smaller than usual in the present case. It is equally probable though that some of the assumptions (*e.g.*, that the transition state has the same amount of carbanion character for each haloform) that are implicit in eq. 3 are incorrect, and that for this reason our parameters may contain other factors in addition to those they were designed to measure. It therefore seems best not to attach too much significance to such small differences as those between our $N$-values.

The fact that $c$ is larger than $d$ ($c - d$ is positive) suggests that the trihalomethyl anions have lost more carbanion character in the transition state for their transformation to haloform than they have in the transition state leading to dihalomethylene. This is perhaps not surprising, particularly in view of the fact that considerable carbanion character still remains in the dihalomethylene (assuming a singlet state). The values of the parameters obtained are not precise enough to show with any certainty the relative extents to which they reflect entropy and enthalpy effects. It is worthwhile to point out, though, that parameters due solely to enthalpy effects should decrease in absolute value by 18% (323/273 = 1.18) between 0 and 50°, as our $M$-values tend to do, while entropy factors should remain constant.

**Correlation in Methanol and Dioxane–Water.**—A comparison of the data of Table I with the rate constants for hydrolysis in 66²/₃% dioxane–water already published[3] shows that the change in solvent has a variable effect on the reaction rates. Thus while chloroform hydrolyzes at about the same rate in the two solvents, dichloroiodomethane hydrolyzes more than three times and bromochlorofluoromethane more than ten times as fast in two-thirds dioxane. To compare a completely nonaqueous solvent we studied the reaction with sodium methoxide in methanol and found that chloroform reacted only about one-seventieth as fast as in water. Since the assumptions involved in deriving eq. 3 depended only on the mechanism of the formation of the dihalomethylene and not upon the solvent used, the equation should fit data in solvents other than water so long as no change in reaction mechanism occurs. For this reason we have determined rate constants for the basic hydrolysis of several haloforms (including iodoform, for which we had no data in water) in addition to those studied previously in 66²/₃% dioxane–water and for the basic methanolysis of four haloforms in methanol. Hughes and Peeling have previously found that bromoform is readily alcoholized by mechanisms of a homolytic character, but that these mechanisms can be excluded and, when they are, the reaction with methoxide ions is kinetically second order.[30] In agreement with this observation we found that the second-order rate constants for the reaction of bromoform with methanolic sodium methoxide varied quite widely within a given run and between different runs even when the runs were carried out under "commercial nitrogen." In the presence of 0.26% diphenylamine, however, the rate constants were reproducible and within the experimental error of those obtained with 1.2% diphenylamine, showing that the inhibition was complete. Apparently the tendency for free radical reactions to intervene increases with increasing molecular weight of the haloform and is greater in methanol than in dioxane–water. The methanolysis rate of dibromochloromethane was not slowed by the addition of diphenylamine and neither were the hydrolysis rates of bromoform, dichloroiodomethane or chlorodiiodomethane in 66²/₃% dioxane–water. The hydrolysis of iodoform in dioxane–water, however, was slowed several fold by diphenylamine. The second-order rate constants obtained for the basic decomposition reactions in methanol and dioxane–water are listed in Table IV.

TABLE IV

KINETIC CONSTANTS FOR THE BASIC DECOMPOSITION OF HALOFORMS

| Haloform | $10^4k$, l. mole$^{-1}$ sec.$^{-1}$ 35.0° | 50.0° | $\Delta H^\ddagger$, kcal./mole | $\Delta S^\ddagger$, e.u. |
|---|---|---|---|---|
| | In dioxane–water | | | |
| $CHCl_2I$ | 39.9 ± 0.4[a] | 293 ± 5[b] | 27.1 ± 1.0 | 18.3 ± 3 |
| $CHClI_2$ | 180 ± 10[c] | 17.7 ± 0.4 | 29.0 ± 1.2 | 18.4 ± 4 |
| $CHI_3$ | 28.7 ± 3[b,d] | 1.55 ± 0.15[b,e] | 29.7 ± 1.5 | 15.6 ± 5 |
| | In anhydrous methyl alcohol | | | |
| $CHCl_3$ | 0.306 ± 0.005 | | | |
| $CHBrCl_2$ | 9.25 ± .05 | | | |
| $CHBr_2Cl$ | 6.30 ± .08 | | | |
| $CHBr_3$ | 2.41 ± .09[b] | | | |

[a] Data from ref. 3. [b] In the presence of diphenylamine. [c] At 67.1°. [d] At 71.3°. [e] Rate constant determined graphically.

In order to test eq. 3 for solvents other than water, some modifications are required, since no kinetic studies of deuterium exchange of haloforms in solvents other than water appear to have been reported. For those haloforms that do not contain fluorine, in water $k_2$ is so small compared to $k_{-1}$ that the relation

$$k_2/k_{-1} = k_h/k_1 \qquad (5)$$

(29) (a) H. Böhme, H. Fischer and R. Frank, *Ann.*, **563**, 54 (1949); (b) J. B. Conant, W. R. Kirner and R. E. Hussey, THIS JOURNAL, **47**, 488 (1925); P. D. Bartlett and L. J. Rosen, *ibid.*, **64**, 543 (1942); (c) D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A211**, 254 (1952); (d) B. V. Tronov and E. A. Krüger, *J. Russ. Phys.-Chem. Soc.*, **58**, 1270 (1926); (e) H. J. Backer and W. H. Van Mels, *Rec. trav. chim.*, **49**, 363 (1930); K. A. Cooper, E. D. Hughes, C. K. Ingold and B. J. MacNulty, *J. Chem. Soc.*, 2038 (1948); H. R. McCleary and L. P. Hammett, THIS JOURNAL, **63**, 2254 (1941); G. H. Grant and C. H. Hinshelwood, *J. Chem. Soc.*, 258 (1933); A. Slator, *ibid.*, **85**, 1286 (1904); **87**, 4281 (1905).

(30) Private communication from E. D. Hughes and E. R. A. Peeling quoted by C. K. Ingold, ref. 24, p. 330.

holds very well. For $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ the relation

$$\log \frac{k_1^{CHCl_nBr_{3-n}}}{k_1^{CHCl_3}} = nQ \qquad (6)$$

where $Q$ is a constant (equal to 0.73 at 0°), is a good approximation,[7] assuming that the kinetic isotope effects are the same for all of the haloforms. With the reasonable assumption that these two approximations are also good in methanol and dioxane–water, eq. 5 and 6 may be combined with eq. 3 to give

$$\log \frac{k_h^{CHBr_nCl_{3-n}}}{k_h^{CHCl_3}} =$$

$$\log \frac{n}{3} + n[Q(1 + c - d) + M_{Br}] + (N_{Br} - M_{Br}) \qquad (7)$$

This equation permits the correlation of three data in terms of two parameters. By a least squares treatment the following were calculated as the optimum values for $Q(1 + c - d) + M_{Br}$ and $N_{Br} - M_{Br}$, respectively: for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ in 66⅔% dioxane–water at 35.7°, −0.613 and 2.466; and in methanol at 50°, −0.530 and 2.507; by an analogous treatment for $CHCl_3$, $CHCl_2I$, $CHClI_2$ and $CHI_3$ in 66⅔% dioxane–water at 50°, −1.377 and 2.950. These three sets of values permit the calculation of the three relevant rate constants with average deviations of 3, 7 and 16%, respectively. The difference between these values and the analogous ones that may be calculated from the data for pure water are not sufficient to permit any significant conclusions to be drawn.

## Experimental

**Reagents.**—The methods of purification of chloroform, bromodichloromethane, chlorodibromomethane, bromoform, dichloroiodomethane and dioxane have been described previously.[3] Methanol was purified with magnesium by the method described by Fieser.[31] Reagent iodoform and Eastman Kodak Co. white label diphenylamine were used without further purification. Chlorodiiodomethane was prepared by the method of Auger,[32] 158 g. of crude product and 95 g. of twice-fractionated (under nitrogen) material, b.p. 101–102° (33 mm.) being obtained from 312 g. of iodoform and 100 g. of mercuric chloride.

Some of the dichloroiodomethane was prepared by the method of Auger[32] and some was synthesized in the following manner. A solution of 137 g. (0.9 mole) of sodium iodide and 99 g. (0.6 mole) of bromodichloromethane in 250 ml. of methanol was stirred at reflux while 14 g. (0.35 mole) of sodium hydroxide in 35 ml. of water was added dropwise over a period of 30 minutes. After 15 additional minutes of refluxing, the material was allowed to cool overnight and then water was added, causing separation into two layers. The organic layer was taken up in methylene chloride and combined with a hexane extract of the aqueous layer. After the methylene chloride and hexane had been removed by distillation through a 30-inch column at atmospheric pressure, the pressure was reduced to 110 mm., where 61 g. of dichloroiodomethane ($n^{23}D$ 1.5810) was collected between 73 and 74°. In addition to the 49% yield in this main fraction 8% was obtained in fore- and after-runs within 5° of it.

"Oxygen-free" water was prepared by boiling distilled water and cooling it under nitrogen or by bubbling nitrogen through the water for a prolonged period. Carbonate-free sodium hydroxide was made by dilution of a filtered ~20 $M$ solution.

**Kinetic Runs.**—Our temperature-control methods have been described previously.[3] Kinetic runs were carried out by several different methods. In method A a known volume of a standard solution of haloform in the appropriate solvent or solvent-mixture was thermostated in a volumetric flask, and at zero time a thermostated standard solution of base was pipeted into the flask. In the cases of most reactions at 50° and above, and those reactions at 20° and above that required several days to run, samples were pipeted from the reaction flask into a flask containing some clean ice, and the unreacted base was titrated with standard acid (either hydrochloric or perchloric). For purely aqueous or aqueous dioxane solutions phenolphthalein was used as the indicator. In methanolic solutions either *p*-nitrophenol or curcumin (turmeric yellow) was used. In other reactions the reaction sample was pipeted into a known volume (excess) of standard acid and the excess acid back-titrated. All operations except the final titration were carried out under nitrogen. Method B was a modification of A in which a small volume of ~5 $N$ sodium hydroxide solution was added by syringe at zero time. The initial base concentration was calculated by extrapolation from several points taken as soon as possible. Method C resembled A except that a number of flasks containing standard haloform solutions were made up and a known volume of base added to each at zero time. To take a point, the entire contents of a flask were poured onto ice or into an excess of acid and the flask was rinsed twice with distilled water. In runs where diphenylamine was used, it was weighed out with the haloform.

Method A was used for studying the hydrolysis of dibromochloromethane at 0° and of bromodichloromethane at 35° in aqueous solution. Method C was used for the hydrolysis of chloroform in water, dichloroiodomethane in aqueous dioxane and in water at 35°, and iodoform in aqueous dioxane. Method B was used for all of the other reactions except those on which the data are quoted from other articles.[6-8]

**Calculations.**—Rate constants were calculated by use of the second-order rate equation employed previously

$$kt = \frac{2.303}{(3 + f)a - b} \log \frac{a(b - x)}{b(a - [3 + f]x)} \qquad (8)$$

where $a = [CHX_3]_0$, $b = [OH^-]_0$ or $[OMe^-]_0$, $x = \Delta[CHX_3]_t$, $t$ = time (sec.), and $3 + f$ is the number of moles of base that react per mole of haloform, $f$ being the fraction of haloform that produces formate in cases where carbon monoxide and formate ions are the only products. Although it is difficult to determine $f$ very accurately, fortunately, the value of $k$ obtained is rather insensitive to the value of $f$ used in the calculation. Since the values of $f$ obtained for chloroform at various temperatures in water and aqueous dioxane did not vary beyond the rather considerable experimental error (in determinations in which the halide and hydroxide ion concentrations were measured) we used the value 0.15, obtained previously,[14] in all calculations on chloroform in water-containing solvents. Since the value of $f$ should depend only on the nature of the dihalomethylene intermediate, the value 0.15 also was used for bromodichloromethane and dichloroiodomethane whose hydrolysis, like that of chloroform, proceeds through dichloromethylene as an intermediate. For bromoform and dibromochloromethane in aqueous solvents a value of 0.08 was used, since a number of determinations showed this value to be very probably within a factor of two of the correct value. For all of the runs in methanol and for iodoform and chlorodiiodomethane in aqueous solvents, a value of zero was used for $f$ since the values obtained experimentally were quite low (sometimes negative) and poorly reproducible.

In some cases the rate constants calculated from eq. 8 fell (never so much as 20%) as the reaction proceeded. In these instances (noted in Tables I and III), which may have been due to the presence of such reactive impurities as carbonyl halides, the rate constants were determined from the slope of plots of the right-hand side of eq. 8 *vs.* $t$.

Heats and entropies of activation listed were calculated from the absolute rate equation[33]

$$k = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

**Acknowledgments.**—The authors wish to express their gratitude to Dr. Arthur M. Dowell,

(31) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., p. 289.

(32) V. Auger, *Compt. rend.*, **146**, 1037 (1908).

(33) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y. 1941, p. 14.

Jr., Mr. Billy D. Oakes, Mr. Paul B. Langford and Mr. Franklin P. Prosser, each of whom determined one or two of the rate constants reported herein; to the Rich Electronic Computer Center for use of their equipment; and to Dr. Bertram M. Drucker for instruction in computer techniques.

ATLANTA, GEORGIA

GEORGIA INSTITUTE OF TECHNOLOGY

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Technical Report No. 5

# METHYLENE DERIVATIVES AS INTERMEDIATES IN POLAR REACTIONS. XV. THE DECOMPOSITION OF DICHLOROFLUOROACETIC ACID.

Contract No. DA-01-009-ORD-431

by

Jack Hine and Donald C. Duffey

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# Methylene Derivatives as Intermediates in Polar Reactions. XV. The Decomposition of Dichlorofluoroacetic Acid

By Jack Hine and Donald C. Duffey

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[Contribution from the School of Chemistry of the Georgia Institute of Technology]

# Methylene Derivatives as Intermediates in Polar Reactions. XV. The Decomposition of Dichlorofluoroacetic Acid[1]

By Jack Hine and Donald C. Duffey

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The kinetics of the decomposition of dichlorofluoroacetic acid have been studied in aqueous solution. All of the observations are consistent with a reaction mechanism involving a first-order decomposition of the dichlorofluoroacetate ion to carbon dioxide and a dichlorofluoromethide ion that is usually protonated to give dichlorofluoromethane but that often (up to 30% of the time) loses a chloride ion to give the intermediate chlorofluoromethylene which is then hydrolyzed to a mixture of carbon monoxide and formic acid.

## Introduction

The decarboxylation of a number of trihaloacetic acids has been shown to be a first-order reaction of the anion that involves the initial formation of carbon dioxide and a trihalomethyl anion that is subsequently protonated to give a haloform.[2-4] A correlation between the rates of carbanion formation by decarboxylation and the rates of carbanion formation from deuteriohaloforms and alkali has been established.[5] In connection with this correlation and a study of the decarboxylation of the chlorodifluoroacetate ion, which appears to be a concerted decomposition to difluoromethylene not involving a carbanion intermediate,[6] we have studied the decarboxylation of dichlorofluoroacetic acid. The reaction has already been investigated briefly by Auerbach, Verhoek and Henne, who reported that solutions of the sodium salt in ethylene glycol at 178° rapidly became acidic with the liberation of fluoride and chloride ions and that below 100° some decarboxylation occurred but that only about 23% of the expected base was produced.[4] These authors then concluded that the acid hydrolyzed more rapidly than it decarboxylated. It seems plausible to us that the reaction is initiated by the carbanion formation characteristic of other trihaloacetic acids, but that a considerable fraction of the intermediate carbanions, unlike those of the acids studied previously (except bromochlorofluoroacetic, which gave poorly reproducible results[3]), decompose to a dihalomethylene instead of being protonated to haloform molecules. Another explanation is that the haloform that is produced may subsequently hydrolyze. It may be noted in this regard that the hydrolytic reactivity of dichlorofluoromethane compared to the decarboxylation rate of the acid from which it is formed is the largest of any acid studied except perhaps bromochlorofluoroacetic. Thus, of course, the subsequent hydrolysis of initially produced haloform becomes more probable in this case.

(1) For part XIV see J. Hine and P. B. Langford, This Journal, 80, 6010 (1958).

(2) F. H. Verhoek, *ibid.*, 56, 571 (1934); R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

(3) L. H. Sutherland and J. G. Aston, This Journal, 61, 241 (1939).

(4) I. Auerbach, F. H. Verhoek and A. L. Henne, *ibid.*, 72, 299 (1950).

(5) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, 79, 1406 (1957).

(6) J. Hine and D. C. Duffey, *ibid.*, 81, 1131 (1959).

## Results and Discussion

The decomposition of dichlorofluoroacetic acid in aqueous solutions at 70–100° was studied both in the presence and absence of an acetate buffer. Infrared measurements on the gaseous products showed that large amounts of carbon dioxide and dichlorofluoromethane and smaller amounts of carbon monoxide were formed. Tests on the reaction solution for oxalate, by the method described elsewhere,[6] were negative, showing that no significant amount of the material had undergone hydrolysis. We thus concluded that the following reaction scheme operates

$$Cl_2CFCO_2^- \longrightarrow Cl_2CF^- + CO_2$$

$$Cl_2CF^- \xrightarrow[H_2O]{H^+} CHCl_2F \qquad (1)$$

$$Cl_2CF^- \longrightarrow Cl^- + CClF$$

$$CClF \xrightarrow{H_2O} HCl,\ HF,\ CO \text{ and } HCO_2H$$

the observed products being formed according to the stoichiometry

$$Cl_2CFCO_2H \longrightarrow CO_2 + CHCl_2F$$

$$Cl_2CFCO_2H + H_2O \longrightarrow 2HCl + HF + CO_2 + CO$$

$$Cl_2CFCO_2H + 2H_2O \longrightarrow 2HCl + HF + CO_2 + HCO_2H$$

Dichlorofluoromethane that is hydrolyzed gives the same stoichiometry as that which decomposes as the carbanion without ever reaching the haloform stage. From the equations above it may be seen that the concentration of chloride ion formed is equal to the following function of the concentration of dichlorofluoroacetic acid that has reacted and the dichlorofluoromethane that has been formed

$$[Cl^-] = 2(\Delta[Cl_2CFCO_2H] - [CHCl_2F]) \qquad (2)$$

Similarly, the change in total acid concentration may be expressed

$$\Delta[H^+] = (2 + f)(\Delta[Cl_2CFCO_2H] - [CHCl_2F]) - [CHCl_2F] \qquad (3)$$

where $f$ is the fraction of the haloform hydrolysis that yields formate; that is

$$f = [HCO_2H]/([CO] + [HCO_2H])$$

From eqs. 2 and 3 the following equation may be obtained for the yield of dichlorofluoromethane

$$\frac{[CHCl_2F]}{\Delta[Cl_2CFCO_2H]} = 1 - \frac{1}{3 + f - 2(\Delta[H^+]/[Cl^-])} \quad (4)$$

Analyses for the formate and carbon monoxide produced gave $f$-values ranging from 0.44 to 0.66. We have used an intermediate value of 0.50 in our calculations. A 20% error in this value will change the calculated dichlorofluoromethane yield by less than 1% in the range of our observations. The calculated yields of haloform (69 ± 6%) are reasonably near that found by direct analysis in one experiment (72%). To calculate the change in dichlorofluoroacetic acid concentration eqs. 2 and 4 were combined to give

$$\Delta[Cl_2CFCO_2H] = \frac{(3 + f)}{2}[Cl^-] - \Delta[H^+] \quad (5)$$

The kinetics of the decomposition of dichlorofluoroacetic acid were studied by heating an aqueous solution of the acid and an acetate buffer in a constant temperature bath and following the changes in acidity and/or chloride ion concentration. Rate constants calculated from eq. 5 and the integrated form of the first-order rate equation remained reasonably constant within a run as shown by a typical example in Table I.

TABLE I

DECARBOXYLATION OF DICHLOROFLUOROACETIC ACID IN AQUEOUS SOLUTION AT 94.8°[a]

| Time, sec. | Ml. 0.1356 $M$ $AgNO_3$[b] | $10^6k$, sec.$^{-1}$ |
|---|---|---|
| 0 | 0.23 | |
| 49,700 | 2.78 | 6.47 |
| 66,270 | 3.53 | 6.63 |
| 134,600 | 5.63 | 6.48 |
| 158,100 | 6.22 | 6.56 |
| 181,100 | 6.65 | 6.50 |
| 231,200 | 7.36 | 6.33 |
| 232,300 | 7.48 | 6.54 |
| | | Av. 6.50 ± 0.07 |

[a] $[Cl_2CFCO_2H]_0 = 0.1619$ $M$, $[NaOAc]_0 = 0.336$ $M$, $\Delta[H^+]/[Cl^-] = -0.18$. [b] Per 15-ml. sample.

From the summary of rate constants obtained under various conditions given in Table II there appears to be no very large salt effect, below concentrations of 1.0 $M$ at least, nor any significant effect produced by changing the initial hydrogen ion concentration by more than 100-fold.

Using the absolute rate equation[7]

$$k = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

a plot of $\log k - \log(kT/h)$ *versus* $1/T$ was made. From the best straight line through these points a heat of activation of 38.3 ± 2 kcal./mole and an entropy of activation of 21 ± 6 e.u. were calculated.

These observations support reaction mechanism 1, which like that of most trihaloacetic acids involves a rate-controlling decomposition of the carboxylate anion to carbon dioxide and a trihalomethyl carbanion. The question of whether the halide ions observed in the reaction arose directly from dichlorofluoromethyl carbanions formed in the decarboxylation reaction or whether some of them are formed by the subsequent hydrolysis of the dichlorofluoromethane is not definitely settled by our experiments. However, since it was found that dichlorofluoromethyl carbanions decompose about 7.8% of the time they are formed at 0° and 9.4% at 20°,[8] it seems possible that 30% decompose at 100° so that it is not *necessary* to postulate the subsequent hydrolysis of the haloform.

TABLE II

DECOMPOSITION OF DICHLOROFLUOROACETIC ACID IN AQUEOUS SOLUTION

| Temp., °C. | Initial ionic strength | $p$H | $10^6k$, sec.$^{-1}$ |
|---|---|---|---|
| 71.3 | 0.77 | 5.02 | 0.18 ± 0.05 |
| 81.0 | 0.08 | 4.70 | 0.78 ± .01 |
| 90.5 | 0.17 | 5.02 | 3.39 ± .19 |
| 90.5 | 0.77 | 5.02 | 3.34 ± .17 |
| 90.5 | 1.37 | 5.02 | 3.25 ± .14 |
| 90.5 | 1.97 | 5.02 | 2.72 ± .06 |
| 94.8 | 0.11 | 4.77 | 7.02 ± .25 |
| 94.8 | .34 | 4.77 | 6.50 ± .06 |
| 94.8 | .89 | 6.25 | 6.97 ± .56 |

In connection with the results obtained when chlorodifluoroacetic acid decomposes in the presence of fluoride ions,[6] the effect of added sodium fluoride on the decomposition of dichlorofluoroacetic acid was studied. Even in the presence of saturated sodium fluoride (about 1.0 $M$) less than 1% of dichlorofluoromethane and fluoroform was produced. It seems unlikely that the fluoride ions were displacing chloride ions from the starting material to form chlorodifluoroacetate to any major extent since the latter decomposes (about as fast as dichlorofluoroacetate) to give around 23% oxalate while we observed less than 0.3% oxalate in the dichlorofluoroacetate decomposition carried out in the presence of sodium fluoride.

## Experimental

**Reagents.**—Dichlorofluoroacetic acid from the Columbia Organic Chemicals Co., Inc., was found to have a neutral equivalent of 147.1 ± 0.8, $n^{24}D$ 1.4181, $d^{24}_4$ 1.565 and was used without further purification. Other reagents have been described previously.[1,5,8]

**Analysis of Gaseous Products.**—In some of the studies a 40-ml. reaction vessel equipped with a gas inlet tube was connected through a short condenser to a gas buret in which mercury was used as the confining liquid. At intervals the gas was flushed with nitrogen from the inlet tube into the buret and then transferred to a 10-cm. infrared gas cell. The gas was then analyzed by infrared measurements at 4.33 $\mu$ for carbon dioxide, 4.64 $\mu$ for carbon monoxide, 8.72 $\mu$ for fluoroform, 8.97 $\mu$ for chlorodifluoromethane and 9.23 and 9.33 $\mu$ for dichlorofluoromethane. Measurements using pure materials showed this analytical method to be reliable within 15% for all of the gaseous products except carbon dioxide (perhaps because of interference by atmospheric carbon dioxide), for which errors up to 40% are possible. In some cases the carbon dioxide was determined by Orsat analysis using 35% KOH solution as the absorbant, prior to the infrared analysis. The KOH solution absorbed some of the dichlorofluoromethane, but this amount could be determined by comparison with an example in which the carbon dioxide was not absorbed before infrared analysis.

(7) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(8) J. Hine and N. W. Burske, THIS JOURNAL, **78**, 3337 (1956).

In one run 4.02 mmoles of dichlorofluoroacetic acid and 8.4 mmoles of sodium acetate in 21 ml. of water was refluxed gently for 62 hours. The gas analysis revealed the presence of 4.0 ± 0.1 mmoles of carbon dioxide, 2.9 ± 0.1 mmoles of dichlorofluoromethane and 0.61 ± 0.05 mmoles of carbon monoxide. Titration of the aqueous solution showed the presence of 1.05 mmoles of chloride, 2.30 mmoles of fluoride[9] and 0.47 mmole of formate.[10] The reacting material is thus accounted for essentially quantitatively.

**Kinetic Runs.**—In a typical run, 250 ml. of aqueous solution, 0.1619 *M* in dichlorofluoroacetic acid and 0.336 *M* in sodium acetate, was placed in a 250-ml. volumetric flask in a constant temperature bath at 94.8 ± 0.1°. At intervals, 15-ml. samples were withdrawn and titrated for chloride by the Mohr method. Acidimetric titrations carried out at the end of the run showed that the fraction $\Delta[H^+]/\Delta[Cl^-]$ was −0.18. In other runs in which acidimetric titrations were made at every point it had been found that this ratio remains essentially constant throughout the reaction. The data obtained in this run are given in Table I.

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ATLANTA, GA.

(9) By the method of I. M. Kolthoff and E. B. Sandell, "Quantitative Inorganic Analysis," 3rd ed., The Macmillan Co., New York, N. Y., 1952, p. 721.

(10) By the method of J. W. Hopton, *Anal. Chim. Acta*, **8**, 429 (1953).

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# METHYLENE DERIVATIVES AS INTERMEDIATES IN POLAR REACTIONS. XVI. THE DECOMPOSITION OF DICHLOROFLUOROACETIC ACID.

Contract No. DA-01-009-ORD-431

by

Jack Hine and Donald C. Duffey

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# Methylene Derivatives as Intermediates in Polar Reactions. XVI. The Decomposition of Chlorodifluoroacetic Acid

By Jack Hine and Donald C. Duffey

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# Methylene Derivatives as Intermediates in Polar Reactions. XVI. The Decomposition of Chlorodifluoroacetic Acid[1]

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The decarboxylation of chlorodifluoroacetate ion (unlike most trihaloacetate ions, which lose carbon dioxide to give a trihalomethyl anion) appears to be a concerted decomposition to carbon dioxide, chloride ion and difluoromethylene. This is shown by the fact that very little chlorodifluoromethane is formed, even in acidic solution, and even this small amount appears to come from difluoromethylene rather than from a trihalomethyl anion. Fluoroform is also produced and its yield may be greatly increased if fluoride ion is added to the decarboxylation reaction solution. The addition of chloride ion increases the yield of chlorodifluoromethane, and bromide and iodide ions bring about the formation of bromodifluoromethane and difluoroiodomethane, respectively. Further evidence for the concerted character of the decarboxylation is provided by the rate constant for the reaction which is about forty times as large as would be expected for a decomposition to the chlorodifluoromethide ion. The decarboxylation reaction is accompanied by the formation of oxalic acid by a process that appears to be initiated by the SN2 attack of water on the chlorodifluoroacetate ion. An analogous SN2 attack by fluoride ion to give trifluoroacetate becomes another important side reaction in the presence of 1 *M* or stronger fluoride ion.

## Introduction

Evidence presented in earlier articles in this series shows that the basic hydrolysis of a number of haloforms proceeds by the mechanism

$$CHX_3 + OH^- \rightleftarrows CX_3^- + H_2O$$
$$CX_3^- \longrightarrow CX_2 + X^-$$

followed by rapid reactions of the intermediate dihalomethylene.[2] Subsequent work has shown that while bromodifluoromethane and chlorodifluoromethane also react through dihalomethylene intermediates,[3] their hydrolyses seem much too fast to involve the corresponding trihalomethyl anions.[4] Instead, it appears that the relatively unstable carbanions are by-passed in a concerted $\alpha$-elimination that leads *directly* to difluoromethylene, the most stable of the dihalomethylenes.[5] The concerted mechanism is further supported by the observation that the basic hydrolysis of deuteriobromodifluoromethane, unlike that of the nine other deuterohaloforms studied, is *not* accompanied by deuterium exchange.[4] This observation is permissive but not compelling evidence for the concerted mechanism. The two-stage mechanism could always be supported by the argument that the carbanion is indeed a true reaction intermediate but that under the basic conditions employed for hydrolysis it is reprotonated much more slowly than it undergoes loss of a halide ion. This objection may, of course, be made to the use of deuterium exchange as a test for carbanion intermediacy in any base-catalyzed reaction. However in the present case we have at least partially met this objection by attempting to generate the intermediate carbanion, if indeed there is one, in acidic solution. This was accomplished by studying the decarboxylation of chlorodifluoroacetic acid.

Verhoek[6] and also Fairclough[7] have described evidence that the decarboxylation of trichloroacetic and tribromoacetic acids is a unimolecular decomposition of the carboxylate anion to give a trihalomethyl anion that is subsequently protonated.

$$X_3CCO_2^- \longrightarrow CO_2 + CX_3^-$$
$$CX_3^- \longrightarrow CHX_3$$

Later work supports this mechanism for dibromochloro-[8] and trifluoroacetic[9] acids. There is definitely a qualitative relationship between the reactivity of trihaloacetates in decarboxylation and of deuteriohaloforms in deuterium exchange, another

(1) For part XV see ref. 24. This work was preliminarily described at the Sixth Biennial Conference on Reaction Mechanisms, Swarthmore, Penna., September 13, 1956.

(2) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., THIS JOURNAL, **78**, 479 (1956).

(3) J. Hine and J. J. Porter, *ibid.*, **79**, 5493 (1957).

(4) J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957).

(5) J. Hine and S. J. Ehrenson, *ibid.*, **80**, 824 (1958).

(6) F. H. Verhoek, *ibid.*, **56**, 571 (1934).

(7) R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

(8) L. H. Sutherland and J. G. Aston, THIS JOURNAL, **61**, 241 (1939).

(9) I. Auerbach, F. H. Verhoek and A. L. Henne, *ibid.*, **72**, 299 (1950).

trihalomethyl-anion-forming reaction.[10] Since we have hypothesized that as the hydrogen is removed from chlorodifluoromethane the incipient carbanion largely decomposes to dihalomethylene, we should expect the same incipient carbanion arising during decarboxylation also to decompose as it is formed. That is, we should expect the rate-controlling step of the decarboxylation to be a single concerted process leading directly to carbon dioxide, chloride ion and difluoromethylene.

$$ClCF_2CO_2^- \longrightarrow \overset{-\delta}{Cl}\cdots\overset{-\delta}{CF_2}\cdots\overset{-\delta}{CO_2} \longrightarrow Cl^- + CF_2 + CO_2$$

If this mechanism is correct, then unlike the typical trihaloacetic acids, chlorodifluoroacetic acid should not yield haloform upon decarboxylation, unless some is formed from the dihalomethylene produced. Auerbach, Verhoek and Henne reported that sodium chlorodifluoroacetate yielded fluoride and chloride ions and acid, but did not tell whether haloform was produced or not.[9] They concluded that hydrolysis of the acid was occurring faster than decarboxylation. Because of the possibility that the halide ions and acid are produced *by* the decarboxylation and the hydrolysis of the dihalomethylene produced, we decided to study the reaction in more retail.

## Results and Discussion

**Reaction Products.**—Since the trihaloacetic acids are relatively strong they exist to a considerable extent as trihaloacetate ions in aqueous solution even when not neutralized. It was therefore convenient to study the decarboxylation in these acidic solutions where the hydrolysis of any haloform produced should be at a minimum. The infrared spectrum of the volatile products of such decarboxylation reactions showed the presence of carbon dioxide, carbon monoxide and formic acid and small amounts of chlorodifluoromethane and fluoroform. Since Haszeldine has reported that silver chlorodifluoroacetate decomposes in aqueous solution to give oxalic acid in good yield,[11] we tested for oxalate formation in our reaction mixtures. Upon finding a positive test we worked out a semi-quantitative method for analyzing for the oxalate in our reaction solutions, by initial precipitation as silver oxalate, transformation to dimethyl oxalate by the action of methyl iodide and infrared analysis. In runs carried out in the presence of large concentrations of fluoride ion, trifluoroacetic acid was also produced. This was established by a method based on the fact that the trifluoro- acid decarboxylates much more slowly than the chlorodifluoro- acid. The solution to be analyzed was first heated under conditions sufficient to decarboxylate essentially all of the chlorodifluoroacetic acid and then shown to give large amounts of fluoroform when heated to the temperatures at which trifluoroacetic acid is known to decarboxylate readily.

The yields of haloform from the decarboxylation reaction (that is, based on the carbon dioxide formed simultaneously) of 3.3 millimoles of chlorodifluoroacetic acid in 25 ml. of water at gentle reflux for 11 to 24 hours are shown in Table I.

TABLE I

YIELDS OF HALOFORMS IN THE DECARBOXYLATION OF CHLORODIFLUOROACETIC ACID IN AQUEOUS SOLUTION

| Added salt | Haloform yield, % $CHClF_2$ | $CHF_3$ |
|---|---|---|
| None | 1 | 3 |
| 1.2 *M* NaF | 0.1 | 23 |
| 2.6 *M* NaCl | 8 | 0.1 |

Just as these quantitative experiments showed that sodium fluoride increased the fluoroform yield and sodium chloride increased the chlorodifluoromethane yield, qualitative experiments showed that the addition of lithium bromide and of sodium iodide brought about the formation of bromodifluoromethane and difluoroiodomethane, respectively.

In acetate-buffered ($p$H 4–5) solutions the yield of oxalate was 22 ± 4% while in the more acidic ($p$H ~1) unbuffered solutions it was about 43%.

**Reaction Kinetics.**—Believing that the decarboxylation of chlorodifluoroacetic acid would prove to be a first-order reaction of the anion, like that of other trihaloacetic acids has been found to be,[6-9] we studied the reaction kinetics in a solution containing a sodium acetate–acetic acid buffer. In a strongly acidic solution the kinetics might have been complicated by the presence of considerable amounts of chlorodifluoroacetic acid in its un-ionized form, while in a basic solution any chlorodifluoromethane that was produced might be lost by subsequent hydrolysis. One chloride ion is liberated for every chlorodifluoroacetate ion that reacts by any of the paths except the one that leads to chlorodifluoromethane. Since very little of this haloform is produced, particularly in the dilute solutions on which we made kinetic studies, the over-all rate of decomposition of chlorodifluoroacetate may be followed satisfactorily by titration of the chloride ions liberated. The reaction may also be followed acidimetrically. Except in those runs where sodium or potassium fluoride was added with the result of a large amount of attack on the walls of the glass reaction vessel, the ratio of the change in acidity to the concentration of chloride ions formed remained essentially constant throughout the reaction. This is expected since the concentrations of halide ions liberated in the dilute solutions used are not sufficient to bring about any major change in the fractions of reaction proceeding by the various paths. Thus kinetic runs were made by acidimetric measurements on each point, coupled with enough chloride determinations to give the ratio accurately. The ratio was found to be little affected by the $p$H over the range studied (1 to 5). In the runs made in the presence of large concentrations of sodium chloride and bromide the ratio could not be determined at all accurately and was therefore assumed to be the same as in similar runs without added salt. A correction for the amount of additional haloform probably produced in these cases would raise the rate constants by no more than 8%.

(10) J. Hine, N. W. Burske, M. Hine and P. B. Langford, THIS JOURNAL, **79**, 1406 (1957).

(11) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

Despite the presence of the buffer the hydrogen ion concentration changed by several-fold in most of our kinetic runs. Therefore the constancy of the rate constants obtained within the various runs is good evidence that the present process is a first-order reaction of the carboxylate anion.

The rate constants obtained under the various conditions used are summarized in Table II. Infrared measurements showed that in the presence of the acetate buffer about 3% of a mixture of chlorodifluoromethane and fluoroform was produced, much as had been observed (Table I) with the unbuffered solution. From a plot of log $k$ − log ($kT/h$) *vs.* $1/T$ based on Table II, a heat of activation of 32 ± 2 kcal./mole and an entropy of activation of +3 ± 3 e.u. may be calculated for the decomposition reaction as a whole. If the fraction of the reaction that involves hydrolysis to give oxalate is independent of the temperature, the activation parameters for the decarboxylation

TABLE II

RATE CONSTANTS FOR THE DECOMPOSITION OF CHLORODIFLUOROACETIC ACID IN AQUEOUS SOLUTION[a]

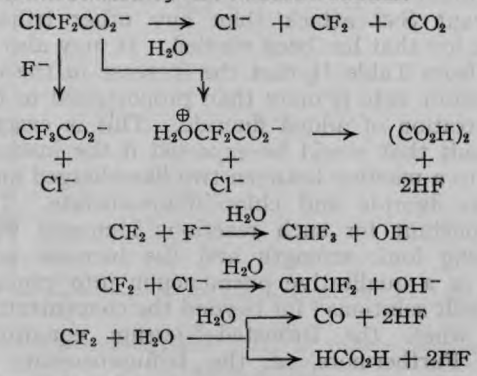
| Temp., °C. | Added salt | $10^5k$, sec.$^{-1}$ |
|---|---|---|
| 97.2 | None | 2.0 ± 0.2 |
| 97.1 | None | 1.84 ± .02 |
| 71.6 | None | 0.129 ± .003 |
| 97.2 | 1.2 *M* NaF | 4.4 ± .1 |
| 97.3 | 0.95 *M* NaF | 3.5 ± .5 |
| 94.9 | 2.3 *M* KF | 9.4 ± 1.1 |
| 97.3 | 0.8 *M* NaBr | 2.2 ± 0.1 |
| 97.2 | 1.64 *M* NaCl | 1.94 ± 0.08 |

[a] An acetate buffer was also present in each case to keep the *p*H between 4 and 5.5.

reaction are essentially the same. The change in the ratio of acid to chloride formed in the experiments at lower temperatures suggested that the oxalate yield was increasing, but direct determinations showed a small decrease.

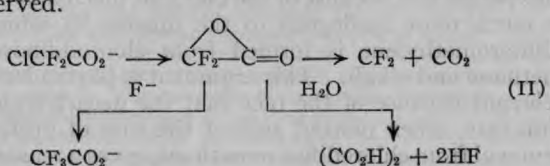
**Reaction Mechanism.**—The data of Table I, on the yields of the volatile products in the presence and absence of added salts, provide good evidence that the decarboxylation of chlorodifluoroacetate is a concerted process, yielding difluoromethylene directly without the intervention of a trihalomethyl carbanion. The relative absence of chlorodifluoromethane from the reaction products was not due to hydrolysis of this haloform after it was produced. Separate experiments showed that the hydrolysis of this compound in aqueous solution is so slow that little of it would have been destroyed under the reaction conditions. The fluoroform observed could not have been formed from trifluoroacetic acid present as an impurity or formed during the reaction because separate experiments showed that trifluoroacetic acid decarboxylates too slowly to yield an observable amount of fluoroform under our reaction conditions. Nor is it possible that the fluoroform is produced by the reaction of chlorodifluoromethane with fluoride ions. Independent experiments showed that this process would never be more than a minor reaction under the conditions used.

It appears that even that small amount of chlorodifluoromethane that is formed arises, at least largely, from difluoromethylene molecules and chloride ions produced in the decarboxylation reaction. Most of the intermediate $CF_2$ molecules are hydrolyzed to yield fluoride ions that combine with some of the $CF_2$ to produce the fluoroform observed. This explanation for the formation of fluoroform is supported by the sharp increase in fluoroform yield that occurs in the presence of added fluorides and by the independent observation that in the presence of fluoride ions the reaction of chlorodifluoromethane with alkali, another process in which difluoromethylene is formed, yields fluoroform. We believe that our data are accommodated by the reaction scheme




Except in those runs made in the presence of large concentrations of fluoride ions, the principal reaction path is a concerted decarboxylation to difluoromethylene, which reacts subsequently as shown. The second reaction path shown is simply a solvolysis reaction in which the nucleophilic solvent water displaces a chloride ion by what seems best classified as an SN2 reaction.[12] The intermediate thus formed then undergoes a number of rapid reactions to yield oxalic and hydrofluoric acids. The chlorodifluoroacetate ion is also susceptible to nucleophilic attack by fluoride ion, and the third primary reaction path, which becomes important only in the presence of considerable concentrations of fluoride ion, consists of this reaction, leading to the trifluoroacetate ion.

An alternate reaction scheme in which the initial step of the reaction is the formation of an $\alpha$-lactone (or as Ingold prefers to consider it, a carbonium ion whose configuration is maintained by interaction with the carboxylate anion group[13]) which then reacts further with the available nucleophilic reagents, or decomposes to $CF_2$ and $CO_2$, would also explain the reaction products that we have observed.




However this reaction mechanism seems to be rendered implausible by our kinetic results. Thus, according to this reaction mechanism, fluoride

(12) For a discussion of the SN2 and SN1 mechanisms see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 93–113.

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 383–384.

ion may intercept an intermediate to produce trifluoroacetate but it cannot change the total rate of disappearance of chlorodifluoroacetate, except by a salt effect. The increases in decomposition rate brought about by the addition of sodium and potassium fluorides (Table II) seem altogether too large to be merely "salt effects." These increases are quite reasonably interpreted in terms of an SN2 attack of fluoride ion on the chlorodifluoroacetate molecule (scheme I). It is known that as $\alpha$-substituents fluorine atoms decrease SN2 reactivity less than any other halogen.[14] This fact coupled with its relatively low decomposition rate makes the chlorodifluoroacetate ion more likely to undergo significant SN2 attack than any other trihaloacetate ion that has been studied. It may also be noted from Table II that the increase in the decomposition rate is more than proportional to the concentration of added fluoride. This is exactly the result that would be expected if the increase is due to a reaction between two like-charged ions, such as fluoride and chloridifluoroacetate. The rate constant for such reactions increases with increasing ionic strength and the increase continues as a qualitative phenomenon into concentrated salt solutions[15] far beyond the concentration range where the Brönsted–Bjerrum equation[16] holds. Furthermore, if the trifluoroacetate is formed by the combination of $\alpha$-lactone with fluoride ions then we might expect that the lactone would also combine with chloride ions and slow the reaction rate by a "mass-law effect" like that established by Grunwald and Winstein in the solvolysis of the $\alpha$-bromopropionate anion.[17] That no mass-law effect was found is added evidence that fluoride ions attack chlorodifluoroacetate ions by an SN2 mechanism.

Since the bromide ion is usually more nucleophilic than the fluoride ion[18] we would expect it to attack the chlorodifluoroacetate ion much faster, with the formation of the bromodifluoroacetate ion. Since this ion should then decompose much more rapidly than the chlorodifluoroacetate ion, the addition of bromide ion should catalyze the reaction. Yet the data in Table II show that any such catalytic action is minor, at best. Apparently, for some reason the fluoride ion is more nucleophilic than bromide toward the chlorodifluoroacetate ion.

The data on the effect of added halide ions thus seem best explained without the hypothesis of an intermediate $\alpha$-lactone. We prefer mechanism I for the formation of difluoromethylene, both for this reason and because of the fact that mechanism I is much more analogous to the process by which difluoromethylene is formed from chlorodifluoromethane and alkali. This argument is particularly relevant because of the fact that the decarboxylation rate, when plotted against the rate of proton removal from chlorodifluoromethane, gives a reasonable fit to the relationship[10] obtained from data on other trihaloacetic acids and haloforms.

Since none of our observations appear to require the $\alpha$-lactone mechanism, while the SN2 mechanism for the reaction of chlorodifluoroacetate with fluoride ion seems established, we also prefer the SN2 mechanism to explain the hydrolysis reaction to give oxalate. The increase in yield of oxalate in acidic solution is presumably due to the fact that chlorodifluoroacetic *acid* can undergo SN2 attack by water but it cannot react by the decarboxylation path.

It should be noted that if the concerted mechanism is considered established for the hydrolysis[4] of $CHBrF_2$ and $CHClF_2$, then the formation of these haloforms from $CF_2$ and the corresponding halide ion in aqueous solution must, according to the principle of microscopic reversibility, not proceed through an intermediate trihalomethyl anion. It must instead be a concerted reaction, in which the carbon atom of $CF_2$ accepts a proton from some acid at the same time that it combines with a halide ion. The combination of $CF_2$ with a proton and fluoride ion is probably not a concerted process, though. The fact that fluoroform is produced in essentially quantitative yield in the decarboxylation of trifluoroacetate ion in boric acid-buffered ethylene glycol solution[9] shows that this decarboxylation probably gives a trifluoromethyl anion as a true intermediate. If this is so, then it is very likely that the hydrolysis of fluoroform proceeds by the carbanion rather than the concerted mechanism and therefore the formation of fluoroform from $CF_2$ and fluoride ion is also a two-stage process.

$$CF_2 + F^- \longrightarrow CF_3^-$$
$$CF_3^- + H_3O^+ \longrightarrow CHF_3 + H_2O$$

The occurrence of the two-step mechanism for the hydrolysis of fluoroform is probably a result of the great difficulty with which fluoride ions are ejected from organic molecules.

The fact that fluoride ions are more effective than chloride ions at combining with the intermediate *difluoro*methylene, as shown by the fact that higher yields of fluoroform could be obtained than of chlorodifluoromethane, was rather surprising in view of the fact that the reactivities of the halide ions toward *dichloro*methylene[19] stand in the same order as do their average nucleophilicities in other reactions, $I > Br > Cl > F$.[20] Our data are not adequate to show the relative reactivities of bromide and iodide ions toward $CF_2$, and in any event a quantitative comparison of the relative reactivities of the four halide ions toward $CF_2$ might be difficult to interpret, since it appears that fluoride reacts by a mechanism different from that of the other halide ions. This difference in mechanism does not, in itself, however, explain the greater reactivity of fluoride, since it is the other halogens for which there is, between haloform and difluoro-

(14) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

(15) A. v. Kiss and P. Vass, *Z. anorg. allgem. Chem.*, **209**, 236 (1932); **217**, 305 (1934); *Z. physik. Chem.*, **160**, 290 (1932); A. N. Kappanna, *J. Indian Chem. Soc.*, **6**, 419 (1929); **8**, 541 (1931).

(16) Reference 12, p. 84.

(17) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 841 (1948).

(18) Reference 12, sec. 6-2.

(19) J. Hine and A. M. Dowell, Jr., THIS JOURNAL, **76**, 2688 (1954).

(20) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953). The nucleophilicity constant of 2.0 for fluoride ion[21] was taken from the talk given by C. G. Swain before the 13th National Organic Chemistry Symposium of the American Chemical Society, June 17, 1953, Ann Arbor, Mich.

(21) Reference 12, p. 140.

methylene, a path of *lower* energy than the intermediate carbanion would have. The unexpectedly high nucleophilicity of fluoride ions toward difluoromethylene has already been observed in the reaction of potassium isopropoxide with chlorodifluoromethane where about 5% fluoroform was observed[22] despite the fact that the fluoride ion concentration remains quite small (because of the limited solubility of potassium fluoride in isopropyl alcohol). It seems probable that this nucleophilicity is related to the presence of fluorine atoms on the carbon undergoing nucleophilic attack since we have already mentioned the similar unexpected high rate of attack of fluoride ions on the chlorodifluoroacetate ion. The tendency of even one fluorine substituent to increase the reactivity toward nucleophilic atoms that stand higher in the periodic table relative to nucleophilic atoms of higher atomic weight may also be found in the data on the reactivity of methylene halides. Thus while sodium iodide in acetone and sodium thiophenolate in methanol are respectively 330 and 1450 times as reactive as sodium methoxide in methanol toward methylene bromide, they are only 9 and 23 times as reactive toward fluorobromomethane.[14] This is an added example of the type of phenomena recently discussed by Bunnett.[23]

Another argument for the concerted nature of the decarboxylation of the chlorodifluoroacetate ion may be based on the reaction rate. Since the rates of carbanion formation from haloforms and alkali change smoothly as the nature of the halogen atoms is changed and since there is a semi-quantitative relation between these rates and the rates of decarboxylation of trihaloacetate ions[10] we might expect decarboxylation rates also to change smoothly with the structure of the trihaloacetate ion. The only available data that are relevant to this point are represented in Fig. 1. Here the rate constants for decarboxylation in water at 70°[6-10,24] (extrapolated from the nearest possible temperature, if necessary) are plotted *vs.* the number of the chlorine atoms of trichloroacetate that have been replaced by other halogens. For the replacement of chlorine by bromine the points fall near a straight line. For the replacement of chlorine by fluorine three points fall near a straight line but chlorodifluoroacetate, it may be seen, reacts about 40 times as fast as would be expected from the carbanion mechanism. Apparently this carboxylate anion does not have to form a chlorodifluoromethide ion. It has available an alternate lower energy path in which carbon dioxide, chloride ion and difluoromethylene are formed in a single concerted step. This argument is analogous to the previous one based on the rates of haloform hydrolysis and deuterium exchange[4] except that in the present case the rate "expected" for chlorodifluoromethide ion formation was estimated by interpolation rather than by extrapolation. The 40-fold augmentation of rate above that expected leaves open the possibility that 2.5% of the reaction may proceed by the carbanion mechanism.

This investigation leaves several questions unanswered, of course. One is why the addition of 2.6 *M* sodium chloride causes the fluoroform yield to drop so sharply although the chloride ions are only reacting with 8% of the available difluoromethylene molecules. Another relates to the fact that the products we studied accounted for only about 80% of the reacted starting material.

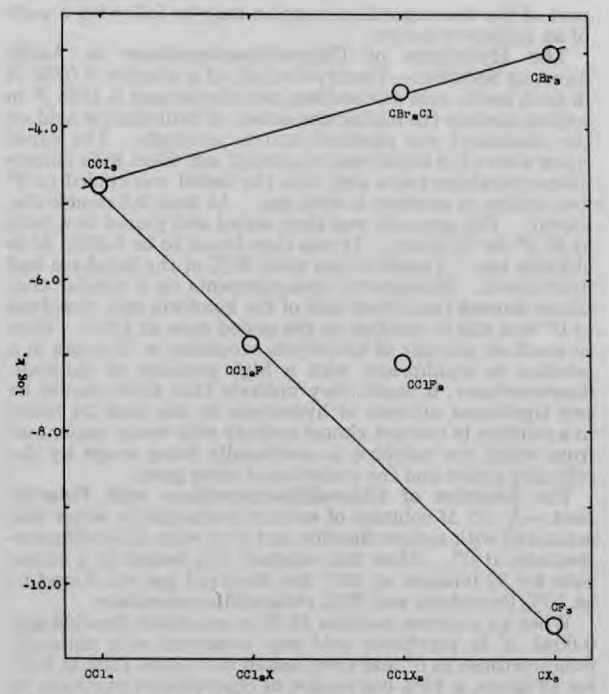



Fig. 1.—Decarboxylation rates of trihaloacetic acids in water at 70°.

## Experimental

**Reagents.**—The chlorodifluoromethane used has been described previously. The chlorodifluoroacetic acid (Columbia Organic Chemicals Co.) used, m.p. 25°, was fractionated (b.p. 114–116° at 740 mm.) before use.

**Decarboxylation of Chlorodifluoroacetic Acid.**—The reaction vessel for this study was a 50-ml. flask into which had been sealed a gas inlet tube fitted with a stopcock. This flask was fitted through a 15-cm. (over-all) reflux condenser to the 100-ml. gas buret of an Orsat gas analysis apparatus. Five runs were made in which 3.3 mmoles of chlorodifluoroacetic acid was used in 25 ml. of aqueous solution. In one run no salt was added, in the second 33 mmoles of sodium fluoride (not all of which dissolved) and in the other three, 66 mmoles of sodium chloride, lithium bromide and sodium iodide, respectively. The reaction flask containing successively the five solutions described was heated with an oil-bath so that its contents refluxed slowly. After a time between 11 and 24 hours, the reaction was discontinued and nitrogen gas was allowed to sweep through the gas inlet tube. The nitrogen and gaseous reaction products, which were collected over mercury in the gas buret, were then admitted to a 10-cm. infrared cell and analyzed as described previously.[24] The presence of bromodifluoromethane and of difluoroiodomethane in the runs with bromide and iodide ions was shown clearly by the spectra, but no quantitative estimates of the yields were attempted. Titrations showed that after 300 hours at 100°, chloride ion was formed from chlorodifluoroacetic acid in 98% yield. In one run, using improved analytical techniques,[24] 67 ± 2% carbon dioxide, 34 ± 3% oxalate, 10 ± 1% carbon monoxide, 24 ± 1% formate, 1 ± 0.2% chlorodifluoromethane, 1 ± 0.2% fluoroform and 68 ± 5% fluoride ion were obtained. Thus the fate of the carboxyl carbon atom was accounted for quantitatively but not that of the α-carbon atom nor of the fluorine. The gas infrared spectra showed no bands except for the compounds reported. It thus seems possible that

(22) J. Hine and K. Tanabe, THIS JOURNAL, **80**, 3002 (1958).
(23) J. F. Bunnett, *ibid.*, **79**, 5969 (1957).
(24) J. Hine and D. C. Duffey, *ibid.*, **81**, 1129 (1959).

part of the decomposition reaction may be following a path of an unknown nature.

**The Hydrolysis of Chlorodifluoromethane in Acidic Aqueous Solution.**—Twenty-five ml. of a solution 0.0752 *N* in both acetic acid and sodium perchlorate and 0.1248 *N* in sodium acetate (to inhibit the action of hydrofluoric acid on the container) was pipetted into an ampoule. The vapor space above the liquid was evacuated and filled with chlorodifluoromethane twice and then the liquid was cooled to 0° and shaken to saturate it with gas. At least 0.5 mmole dissolved. The ampoule was then sealed and placed in a bath at 97.2° for 72 hours. It was then found to be 0.0035 *M* in chloride ion. Therefore less than 20% of the haloform had hydrolyzed. Manometric measurements on a similar container showed that about half of the haloform that dissolved at 0° was still in solution in the sealed tube at 100°. With so small an amount of hydrolysis occurring in 72 hours in a solution in equilibrium with a high pressure of chlorodifluoromethane, it seems very unlikely that there should be any significant amount of hydrolysis in less than 24 hours in a solution in contact almost entirely with water vapor and from which the haloform is continually being swept by the refluxing action and the evolution of other gases.

**The Reaction of Chlorodifluoromethane with Fluoride Ions.**—A 1.6 *M* solution of sodium hydroxide in water was saturated with sodium fluoride and then with chlorodifluoromethane at 0°. After this solution was heated in a sealed tube for 30 minutes at 100° the dissolved gas was found to be 10% fluoroform and 90% chlorodifluoromethane.

When an aqueous solution 10 *M* in potassium fluoride and 0.0043 *M* in perchloric acid was saturated with chlorodifluoromethane at 0° and then heated in a sealed tube at 100° for 48 hours, a 19% conversion of chlorodifluoromethane to fluoroform was observed. Titration of the resultant solution, however, using phenolphthalein, showed that it had become basic to an extent greater than 0.026 *M*. The condition of the walls of the reaction vessel suggested that fluoride ions had been hydrolyzed to hydrogen fluoride which was then destroyed by reaction with the glass. In any case, since the fluoroform formation is obviously base-catalyzed it seems likely that most of the observed 19% of fluoroform was produced after the reaction solution became basic.

**Kinetic runs** were carried out by withdrawing samples of the reaction solutions contained in volumetric flasks immersed in a constant temperature bath. These samples were titrated with standard carbonate-free sodium hydroxide to the phenolphthalein end-point, made slightly acidic with perchloric acid and in some cases then titrated with silver nitrate by Mohr's method. The ratio of the change in acid concentration to the change in chloride concentration did not vary significantly during a run and for this reason the more accurate acidimetric titrations were used in calculating the rate constants. From these titrations and the average value of the ratio $\Delta[H^+]/\Delta[Cl^-]$ the value of $\Delta[ClCF_2CO_2^-]$ was determined, since essentially one chloride ion is formed for every chlorodifluoroacetate ion that reacts. The rate constant was then calculated as shown in Table III, where the data obtained in one run is summarized.

**Analysis for Oxalate.**—Since the fluoride, chloride, formate, acetate or trihaloacetate present seemed to interfere with some of the standard methods for the determination of oxalate, the following new method was devised. A 100% excess of silver nitrate solution was added to the reaction solution and the resultant precipitate of silver chloride, oxalate and perhaps formate was collected on a filter and dried for about 45 minutes at 110°. The dry powder was refluxed with about 20 ml. of methyl iodide for at least an hour and the unreacted methyl iodide was almost entirely removed by fractional distillation. The residue was refluxed with a known volume of carbon disulfide to dissolve the dimethyl oxalate. Some of the clear supernatant carbond disulfide solution was then removed by use of a syringe and the concentration of oxalate therein determined by quantitative measurements on the 5.64 and 5.72 $\mu$ carbonyl bands. Determination of the full spectra showed that the compound being measured was indeed dimethyl oxalate. Blank experiments using reagent sodium oxalate showed that there is some loss of material in the procedure described, but that the yields were 85 ± 10%. Blank experiments were also used to show that neither sodium fluoride, chloride, formate, acetate nor chlorodifluoroacetate interferes with the determination. Oxalate was shown to be stable to even the most acidic conditions employed by a blank experiment in which sodium oxalate was refluxed with 0.03 *M* trifluoroacetic acid for 13 days.

TABLE III

DECOMPOSITION OF SODIUM CHLORODIFLUOROACETATE IN AQUEOUS SOLUTION AT 97.1°

$[ClCF_2CO_2H]_0 = 0.0477$; $[NaOAc]_0 = 0.1355$; $\Delta[H^+]/\Delta[Cl^-] = 2.377$

| Time, sec. | Ml. NaOH 0.04807 *N*[a] | $\Delta[ClCF_2CO_2^-]$ | $10^6k$, sec.$^{-1}$ |
|---|---|---|---|
| 0 | 4.98 | 0.00000 | |
| 21,600 | 5.43 | .00189 | 1.87 |
| 83,400 | 6.61 | .00685 | 1.87 |
| 128,400 | 7.34 | .00992 | 1.81 |
| 173,400 | 8.04 | .01286 | 1.82 |
| 262,200 | 9.37 | .01844 | 1.86 |
| 433,800 | 11.20 | .02612 | 1.83 |
| 527,400 | 12.02 | .02958 | 1.84 |
| | | Av. | 1.84 ± 0.02 |

[a] Per 5-ml. sample.

**Trifluoroacetate from Chlorodifluoroacetate and Fluoride.**—A solution of 14.9 mmoles of chlorodifluoroacetic acid and 21.9 mmoles of sodium acetate in 250 ml. of 2.3 *M* aqueous potassium fluoride was maintained at 94.9° for 92 hours, at which time the titration of an aliquot showed that 89% of the chlorine present had been liberated as chloride ions. A 25-ml. aliquot was neutralized, evaporated to dryness under reduced pressure, dissolved in 25 ml. of ethylene glycol and heated to about 165°. Only carbon dioxide and fluoroform were found in the evolved gases. During the first 2.25 hours 0.3 mmole of fluoroform was evolved, and at the end of this time the rate of gas evolution had not decreased sensibly. The two facts show that the fluoroform must have been coming from trifluoroacetate since the maximum amount of chlorodifluoroacetate present was 0.16 mmole, too small to account for the amount of fluoroform liberated, and the half-life of chlorodifluoroacetate at 165° is only a few minutes, so that any gas evolution from it should quickly stop. The half-life of trifluoroacetate at the temperature, however, is some 20 hours.[9]

**The Decarboxylation of Trifluoroacetic Acid.**—To a solution of 5.0 g. of sodium acetate in 100 ml. of water, 10.4 mmoles of trifluoroacetic acid was added. At various times, 10-ml. samples were withdrawn and titrated with 0.0482 *N* sodium hydroxide solution to the phenolphthalein end-point. At 97.2°, after 122.3 hours, a change in titer of 0.33 ml. had occurred. This corresponds to less than 2% reaction. The presence of 0.65 *M* lithium bromide was found to have no effect on the reaction rate.

**Acknowledgments.**—We wish to acknowledge our indebtedness to the American Viscose Corporation for a fellowship for D. C. D., to the Office of Ordnance Research for the support of this research, and to the "Kinetic" Chemical Division of E. I. du Pont de Nemours and Company for samples of fluoroform and bromodifluoromethane.

ATLANTA, GA.

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## FORMATION OF BIS-(METHYLTHIO)-METHYLENE FROM METHYL ORTHOTHIOFORMATE AND POTASSIUM AMIDE

*Sir:*

Earlier work has provided evidence that a number of trisubstituted methanes, upon treatment with base, undergo $\alpha$-elimination reactions yielding derivatives of methylene as reaction intermediates.[1] There is evidence that the $\alpha$-dehydrohalogenations of bromodifluoromethane, chlorodifluoromethane and difluoroiodimethane are concerted one-step reactions[2] but that the $\alpha$-dehydrohalogenations of chloroform and most other haloforms are stepwise processes involving the formation of small concentrations of reactive intermediate carbanions.[1a,3] We wish now to report that ethyl orthothioformate and methyl orthothioformate, with potassium amide in liquid ammonia, undergo essentially complete transformation to tris-(alkylthio)-methyl anions, which, more slowly, lose thioalkoxy anions to give intermediate bis-(alkylthio)-methylenes, some of which are transformed to tetrakis-(alkylthio)-ethylenes.

Both methyl and ethyl orthothioformate react with potassium amide in ammonia to give green solutions, which are similar in color to those that may be prepared from potassium amide and bis-(methylthio)-methane,[4] but which acquire a brownish color on standing for several hours. Such a solution, prepared from 11.7 g. (76 mmoles) of methyl orthothioformate and 150 mmoles of potassium amide in about 150 ml. of ammonia, was allowed to reflux for an hour before the ammonia was allowed to evaporate. From the residue was isolated 1.8 g. (12 mmoles) of methyl orthothioformate and 2.7 g. (13 mmoles—40% based on unrecovered orthothioformate) of tetrakis-(methylthio)-ethylene, m.p. 59–60°, reported m.p. 61.5°;[6] sole n.m.r.[7] band at 7.63 $\tau$ (in carbon tetrachloride). Tetrakis-(ethylthio)-ethylene, prepared analogously from ethyl orthothioformate, melted at 50–53° and showed no melting-point depression when mixed with tetrakis-(ethylthio)-ethylene prepared from tetrachloroethylene and sodium thioethoxide.[8] In at least one previously reported $\alpha$-elimination the concentration of intermediate carbanion was large enough to observe directly.[9] In the present case there are two observations that show that the reactant is transformed almost quantitatively to its conjugate base. After the addition of one equivalent of potassium amide to solutions of orthothioformates the green color is made no more intense by the addition of further amide. Treatment of a freshly prepared solution of the tris-(methylthio)-methyl anion with methyl iodide leads to the formation of 75% of methyl orthothioacetate, b.p. 98.5–100° (11 mm.), $n^{24.5}$D 1.5680, $d^{24.5}_4$ 1.1197; molecular refractivity calcd. 49.21, found 49.22; sharp n.m.r.[7] absorption band at 8.20 $\tau$ and one with three times the integrated intensity at 7.92 $\tau$ (neat). *Anal.* Calcd. for $C_5H_{12}S_3$: C, 35.67; H, 7.19; S, 57.14. Found: C, 35.49; H, 7.42; S, 57.31.

The fact that tris-(alkylthio)-methyl anions may be generated in high concentrations is to be attributed to the relative ease of removal of a proton from orthothioformates[10,11] and to the difficulty of displacing thioalkoxy anions from saturated carbon atoms. The tetrakis-(alkylthio)-ethylenes formed in the reactions studied need not arise from the dimerization of bis-(alkylthio)-methylenes. They may just as plausibly be ascribed to the reaction of such a methylene with the much more abundant carbanions as shown below.

$$(RS)_3CH + NH_2^- \longrightarrow (RS)_3C^- \longrightarrow RS\text{-}C\text{-}SR + RS^-$$

$$\downarrow (RS)_3C^-$$

$$(RS)_2C{=}C(SR)_2 + RS^- \longleftarrow (RS)_3C{-}C(SR)_2^-$$

In view of the difficulty of displacing thioalkoxy anions from saturated carbon, an alternate mechanism involving the formation of the intermediate pentakis-(alkylthio)-ethane by the nucleophilic attack of tris-(alkylthio)-methyl anions on orthothioformate molecules seems improbable.

**Acknowledgment.**—We wish to acknowledge the support of this investigation by the U. S. Army Research Office (Durham).

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(2) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 5497 (1957); J. Hine and D. C. Duffey, *ibid.*, **81**, 1131 (1959); J. Hine and A. D. Ketley, *J. Org. Chem.*, **25**, 606 (1960).

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(4) We have alkylated such a solution of bis-(methylthio)-methane with propyl bromide and obtained the dimethyl mercaptal of butyraldehyde. The first report of such a reaction was by Arens, Fröhling and Fröhling,[5] who did not state what specific compounds they studied.

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(11) When triphenylmethane is added to a green solution containing two equivalents of bis-(methylthio)-methane per equivalent of potassium amide the solution becomes red. The red color is not discharged by the addition of excess triethyl orthothioformate. We therefore conclude that both of the sulfur compounds are weaker acids than triphenylmethane.

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FINAL REPORT

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JACK HINE

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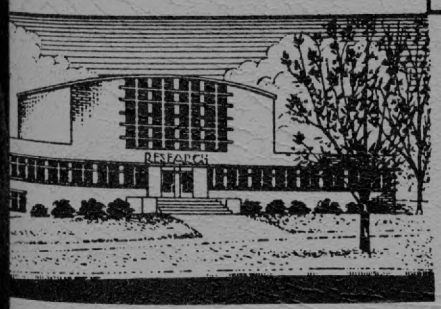

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## FOREWORD

Since essentially all of the work carried out on this contract has been published, it will be reviewed only briefly here but reference will be made to the literature where detailed discussions may be found.

# I. SUMMARY

## Divalent Carbon Derivatives as Reaction Intermediates

A study of the rates of base-catalyzed deuterium exchange of haloforms revealed that the inductive effect of the halogens is not the most important factor in determining the rate of carbanion formation. Instead it was found that as α-substituents halogen atoms facilitate carbanion formation in the order: I ≈ Br > Cl > F.[1]

The reactions of chlorodifluoromethane and bromodifluoromethane with base were found to be initiated by concerted α-dehydrohalogenations,[2] unlike the reactions of most haloforms, in which an intermediate trihalomethyl anion is formed. Dibromofluoromethane and fluorodiiodomethane were found to be highly reactive haloforms but to react by the usual carbanion mechanism.[3]

It was found possible to use a linear free-energy relationship to correlate the relative rates of hydrolysis of the ten haloforms studied whose hydrolyses involve the intermediate formation of trihalomethyl anions. From this correlation it was learned that α-halogen substituents stabilize methylenes in the order F >> Cl > Br > I.[4]

Studies of the decarboxylation of dichlorofluoroacetic acid[5] and chlorodifluoroacetic acid[6] revealed that the former reaction proceeds via an intermediate dichlorofluoromethyl anion but the latter is initiated by a concerted decomposition to carbon dioxide, chloride ion, and difluoromethylene. These observations support the earlier evidence described for the existence of two mechanisms for the basic decomposition of haloforms.

The reaction of chlorodifluoromethane with sodium thiomethoxide in the presence of sodium methoxide was found to involve the intermediacy of methylthiofluoromethylene.[7] The existence of a significant deuterium kinetic isotope

effect in the reaction of $CH_3OCHCl_2$ (and $CH_3OCDCl_2$) with potassium isopropoxide shows that methoxychloromethylene is probably an intermediate in the reaction.[8] An example of the generation of a dihalomethane from a carbanion other than a trihalomethyl anion was found in the reaction of difluoromethyl phenyl sulfone with sodium methoxide, which gave difluoromethylene as an intermediate.[9] Evidence for the formation of bis(methylthio)methylene as an intermediate was found in the reaction of trimethylorthothioformate with potassium amide to give tetrakis(methylthio)ethylene.[10]

It should be mentioned that support from the contract helped Richard Butterworth to get his M.S. in Chemistry; helped Paul B. Langford, Norbert W. Burske, Stanton J. Ehrenson, Donald C. Duffey, John J. Porter, Robert J. Rosscup, and Gary G. Hammer to get Ph.D's in Chemistry; and gave Dr. Raymond P. Bayer some postdoctoral experience.

Respectfully submitted:

Jack Hine
Project Director

Approved:

Frederick Bellinger, Chief
Chemical Sciences and Materials Division

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